NASA TM-86668

NASA Technical Memorandum 86668

Multiplex Gas Chromatography for Use in Space Craft

Jose R. Valentin

January 1985

National Aeronautics and
Space Administration

Technical Memorandum 86668

Multiplex Gas Chromatography for Use in Space Craft

Jose R. Valentin, Ames Research Center, Moffett Field, California

National Aeronautics and
Space Administration

Ames Research Center
Moffett Field, California 94035

N85-18097#

TABLE OF CONTENTS

VII. APPENDICES

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

GAS CHROMATOGRAPHY

History

Chromatography appears to have had its beginning about 1850 in the work of Runge, a German dye chemist, who described a separation process known today as paper chromatography. The earliest reported experiments which can be unequivocally regarded as chromatography are those of Tswett (1), who in 1906 separated the components of plant pigments by passing their solutions through columns of solid adsorbents.

The development of gas chromatography began in the early 1940s (2). Industrial applications involving the adsorption and the desorption of vapors were developed earlier. Basically, adsorption was done at a low temperature, and the adsorbate was desorbed at a higher temperature while purging with a vapor. Eucken and Knick (3) improved this technique in 1936 by using an external oven which was slowly moved along the adsorbent tube. In 1943, Turner (4) combined these techniques and introduced the measurement of the thermal conductivity of the effluent. These early techniques developed into the frontal and displacement methods which were thoroughly studied in the 1940s by Claesson (5) and others at the institute of Tiselius in Upsala, Sweden, and by Phillips (6) and his co-workers at Oxford University in the early 1950s.

During the early 1940s, other work was being done which laid the foundation of modern gas adsorption chromatography. At the University of Marburg/Lahn in Germany, Hesse (7) and his co-workers were using gas adsorption to separate volatile organic acids. This method developed into the new technique of gas adsorption chromatography.

The first modern gas adsorption chromatography was done in 1940 by Cremer at the University of Innsbruck when she began working with a group on the hydrogenation of acetylene and ethylene. She postulated in 1944 that these compounds could be separated by a chromatographic process in the gas phase and that the adsorption energies could be calculated from the elution times (8).

In the 1950s Cremer et al. (9) developed their technique for separation and analysis as well as for the determination of heats of adsorption. They also introduced the ideas of relative retention times, the difference between the retention time and the adjusted retention time, and the determination of peak area from the product of peak height and peak width at half height. They also demonstrated the importance of the logarithm of the adjusted retention time and its relationship to the absolute column temperature (9). In 1952, she exhibited at ACHEMA, the world's largest chemical exhibition in Frankfurt am Main, the first modern gas adsorption chromatograph.

In 1952, Janak (10) developed a chromatograph utilizing carbon dioxide as the carrier gas and a nitrometer as a detector. This initiated considerable interest in the technique of GC. He introduced a two-column system in parallel and in series, and in 1955, he demonstrated the use of zeolites as adsorbents (11).

Liquid-liquid partition as the basis of chromatographic separation was introduced by Martin and Synge (12) in 1941. They won the 1952 Nobel prize for chemistry for this work.

Martin and Synge also proposed the idea of gas-liquid partition chromatography in 1941 but its development did not start until almost 10 years later when James and Martin (13) published their work in 1951. Three more publications in 1952 led to a rapid growth in this separation technique. Improvements, such as the adoption of the thermal conductivity detector used widely in gas adsorption, came rapidly as these and other workers adopted this technique in their laboratories. By 1955, application to a number of problems was demonstrated, and the first commercial instruments were introduced. Over the next 20 years, a rapid advance in GC occurred, which led to its becoming the most widely used analytical technique today.

Gas chromagraphy is a powerful technique for the analysis of gaseous mixtures (14). Besides being a major analytical technique with a great many applications on Earth, including atmospheric analysis, it also has been successfully employed on space missions such as in the Viking Mars lander (15) and the Pioneer Venus probe (16).

Multiplex Gas Chromatography

In the vast majority of gas chromatographic chemical determinations, a discrete pulse of sample is introduced at the head of a chromatographic column. As the sample is carried through the column by a gas stream, it is physically separated into discrete bands by the process of differential migration. At the end of the column the separated bands emerge, each containing a component of the mixture, and are measured by a general purpose chemical or physical detector. Almost all gas chromatographs, including those designed for space applications, followed this conventional organization.

As currently practiced, gas chromatography has two important limitations in atmospheric analysis. First, detector sensitivity is limited by the sample volume. Only small volume samples may be introduced into the column and these samples are further diluted by carrier gas during chromatographic separation. Second, only discrete samples may be accepted. Sufficient time must pass between discrete sample injections for the most strongly retained substance to elute from the column.

Multiplex gas chromatography is a variation of chromatography which solves these problems. Conventional and multiplex GC instruments are compared in Figure 1. In this method the entire gas flow through the chromatographic column may be sampled, and much larger volume samples may be accepted. At the head of the column, each trace component is modulated in concentration to produce a chemical concentration signal. Each modulated substance carries a copy of the modulating signal through the column at its own characteristic migration rate. At the end of the column, a detector measures the sum of all the chemical concentration signals delayed by their retention in the column. The resulting electrical signal, contains information about the quantity and retention of all modulated sample substances multiplexed into every point of the signal. The information is not directly interpretable (see Figure 2), but the equivalent of a chromatogram may be computed from the signal by means of signal detection techniques such as cross correlation.

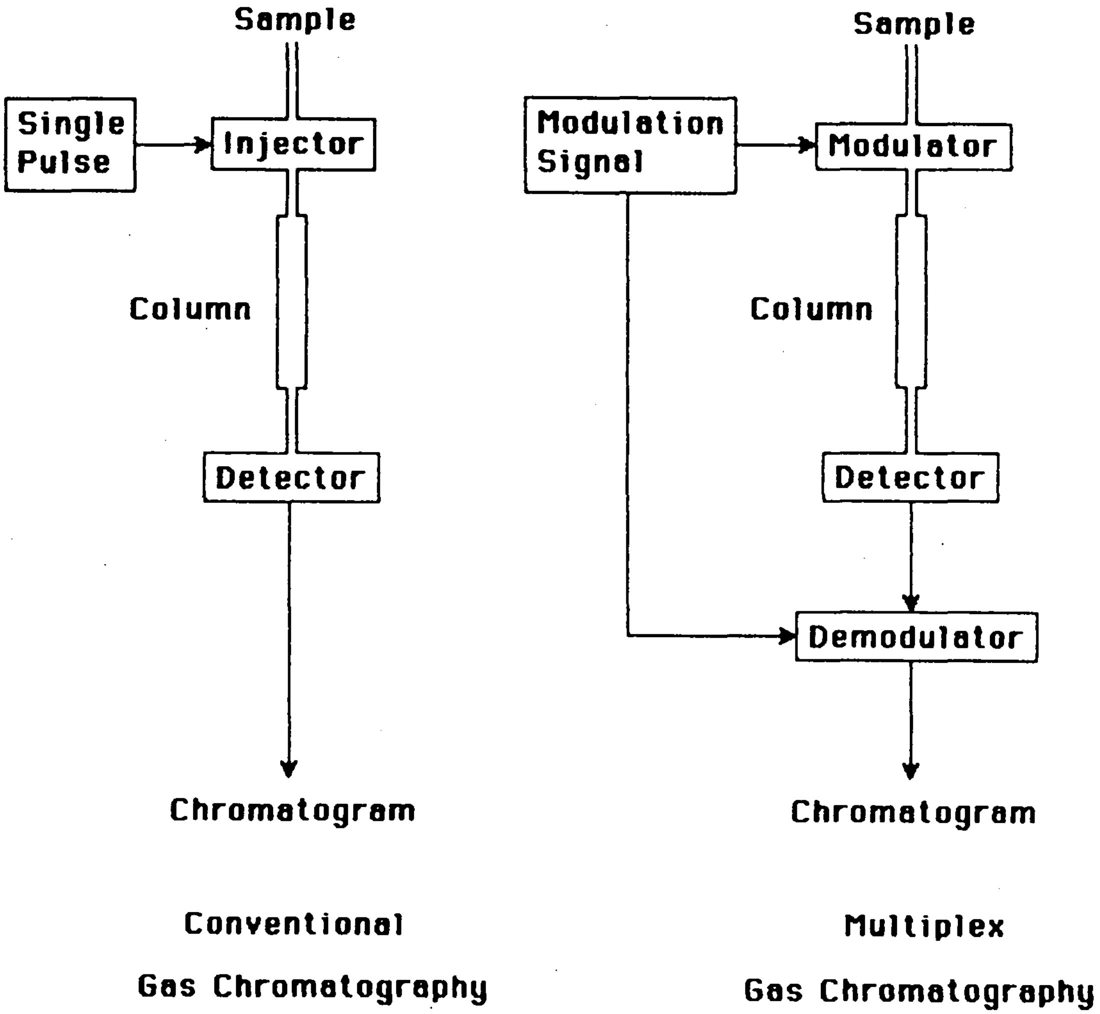

Figure 1

Comparison of multiplex GC with conventional elution GC.

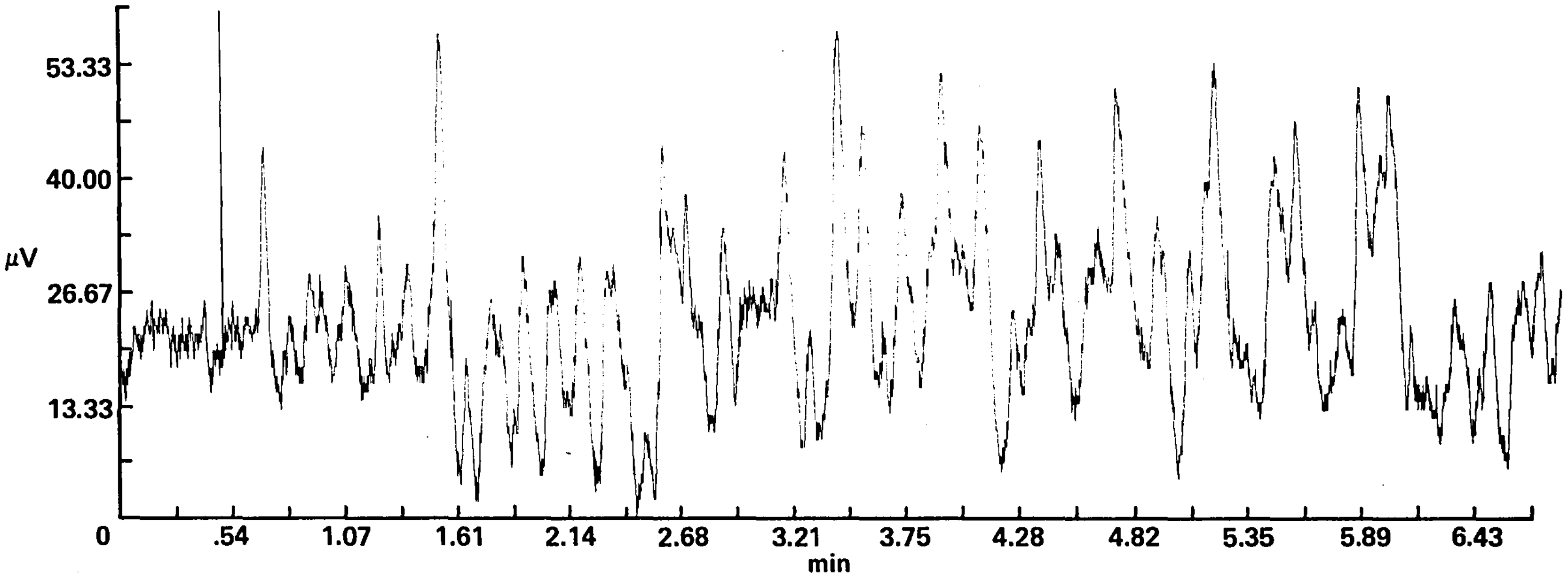

Figure 2

Typical multiplex GC output collected during the first seven minutes of one of the experiments. Chromatographic peaks from different injections are severely overlapped at the detector resulting in an output not directly interpretable by the analyst.

Cross-correlation GC is one example of a multiplex technique applied to chromatographic analysis. In this technique a pseudorandom chemical concentration signal is passed through the column to produce a random output. The cross-correlation is then computed using the following equation:

$$R(T) = (1/N) \sum_{t=1}^{N} \text{input}(t-T) \text{ X } \text{Output}(t)$$

N is the number of data points in the input and output signals, t is discrete time, and T is a delay. For a linear and statistically stationary chromatographic system with a properly chosen input signal, the cross-correlation is identical to the chromatogram except for a possibly improved signal-to-noise ratio.

Multiplex GC offers significant advantages over the conventional elution technique. Some of these advantages are especially important for applications in restricted environments such as on board a space craft.

Sometimes there is only a limited time available to perform an analysis, as for example, in a probe passing through a planetary atmosphere where there is time for analysis of only a few discrete samples taken at points along the trajectory through the atmosphere. No GC information is obtained on the chemical composition of the atmosphere between these points. With multiplex GC, however, there is no need to wait for one determination to be finished before taking a new sample. A new sample may be taken every few seconds and each point of the output signal contains information about all previously taken samples. The precision of any one sample determination is not as good as in a conventional chromatographic technique, but there are a great many more determinations and the total amount of information obtained is much greater.

The detection limit of an analytical method may be limited either by sample concentration or sample quantity. Conventional elution GC is generally limited by quantity. It is usually possible to improve sensitivity at the expense of reduced resolution by taking larger volume samples. Multiplex GC, on the other hand, is limited by sample concentration. As long as there is sufficient volume of sample available, any fraction of the flow through the column up to and including all the flow for an unlimited period of time may be composed of sample. For the analysis of large volume low concentration samples, the multiplex technique can detect orders of magnitude lower concentrations than the conventional single injection technique simply because much more sample is passed through the column to the detector.

Sample preconcentration by cryogenic trapping (17) or by adsorption on a high surface area solid (18) is a common way to improve the sensitivity of conventional GC. A large quantity of sample is collected to provide high sensitivity. The sample is then reduced in volume to match the requirements of the chromatographic system. Multiplex GC can take a comparable quantity of sample and pass it directly to the column eliminating the need for a preconcentration step. Besides simplifying the instrument, this also eliminates the possibility of chemical reactions occurring within the concentrated sample. This can be important in the analysis of chemically reactive atmospheric pollutants.

Weight, volume, power, consumables use, and data transmission rate are all especially important considerations in the design of instruments for space craft use. Multiplex GC offers the possibility of improvements in all of these over what has been achieved by conventional GC. Multiplexed data is more efficiently encoded than discrete chromatograms, so more information can be transmitted in the same number of data bits. If the sample to be analyzed consists of mostly an inert gas with only traces of detectable substances, then the sample might serve as its own carrier gas eliminating the need for a consumable carrier gas. Power, volume, and weight might be reduced through the use of chemical modulators in place of the mechanical gas sampling valves previously used.

Chemical Modulators

In general, a modulator is a device which provides some kind of a change in some physical parameter such as concentration. In conventional elution chromatography, the modulator device is usually a syringe, an injection valve, or a rapidly heated adsorbent, all of which simultaneously introduce the sample and modulate it in the form of a single pulse. The components of the mixture are then separated by their different rates of migration along the column and emerge sequentially at the end of the column. A universal detector may then sequentialy measure the quantity of each separated component.

In multiplex chromatography, the form of modulation is not restricted to a single pulse and many more devices are useful as modulators. Any device which can translate a signal from the electronic domain to the chemical domain is potentially useful. To be useful in chromatography, a modulator should reproducibly generate chemical concentration signals with a high degree of modulation, high concentration gradients, and good linearity.

The degree of modulation of a chemical concentration signal is the fraction of variation above and below the average concentration. In general, it is desirable to maximize the degree of modulation to give the largest signal at the detector. However, it may be necessary to operate at less than maximum degree of modulation in order to raise the frequency of the signal or to keep the modulator and column from nonlinear behavior.

One important contribution to peak resolution in a conventional chromatograph is the sharpness of the initial injection. A sharp injection is a chemical concentration signal in which the concentration change takes place in a short time period. If the time period is short, then the concentration gradients and signal frequencies are large. For the signal at the end of the column (the chromatogram) to contain sharp peaks and high frequencies, the original signal at the head of the column (the injection) must begin with significant power at high frequencies. A sharp injection generates high signal frequencies, but high signal frequencies do not necessarily require sharp injections. Other signal forms contain equally high concentration gradients and, therefore, power at high frequencies. They differ from the sharp injection only in the relative phases of the different frequencies. With mechanical valves high frequencies are usually most easily generated by sharp injections, but for thermal modulators this association does not necessarily exist. It is not necessary for both rising and falling concentration gradients to be large. In principle, either one alone may contribute to the required power at higher frequencies. This fact may be important in thermal modulation where, in practice, heating can usually be done more rapidly than cooling.

Linearity means that a signal behaves as the sum of its component parts. Linearity is a basic assumption of most computational methods used in multiplex chromatography. Within the column, signals carried by different chemical substances must not interfere with each other. Total concentrations must be kept low enough to avoid saturating either the mobile or stationary phase, and the degree of modulation must be limited to avoid more than one retention mechanism. Within the modulator, the generated chemical concentration signal must be a linear function of the applied external signal. Since there are numerous physical and chemical limits on the operation of thermal modulators (for example, the impossibility of negative concentrations), it is easy to make them behave nonlinearly. The simplest way to ensure linearity is to keep the degree of modulation small and avoid approaching any limits. Linearity can also be attained by purposely driving the modulator between two limits. The linearity of detectors is not usually a limiting factor in multiplex chromatography because conventional single injection chromatography places more severe requirements on them.

All previously reported examples of multiplex GC used a valve to alternate between the sample and a reference stream and thus modulate the sample stream. A variety of valves including a rotating seal driven by an air piston (19), a sliding rod driven by a speaker coil (20), a flexible membrane driven by compressed air (21), and a fluidics switch (22) have been used; however, chemical modulators can also be used and may have important advantages in multiplex gas chromatography. A diagram of the type of chemical modulator used in this work is shown in Figure 3.

Thermal Desorption Modulator

Thermal desorption from a chromatographic stationary phase is probably the simplest chemical process that can be used to modulate a sample stream. Modulating the temperature of the stationary phase at the head of a column or in a short precolumn modulates the retention of any retained substances in the sample stream. With a temperature increase, retained components are released from the modulator stationary phase to increase their concentrations in the gas stream at the end of the modulator. With a temperature decrease, retention increases within the modulator reducing concentrations as the stationary phase is refilled. Variation in temperature thus produces variation in concentration in the sample stream. No net sample dilution occurs. Simplification of the instrument has been accomplished by avoiding the use of a reference stream.

Thermal Decomposition Modulator

Modulation by thermal decomposition can also be used to create concentration changes in a continuously flowing sample for analysis by multiplex GC. In this case, the modulator removes thermally unstable components from the sample stream when it is at a high temperature and allows them to pass through when it is at a low temperature. As with the desorption modulator, a variation in temperature results in a variation in concentration. This type of modulation is a simple

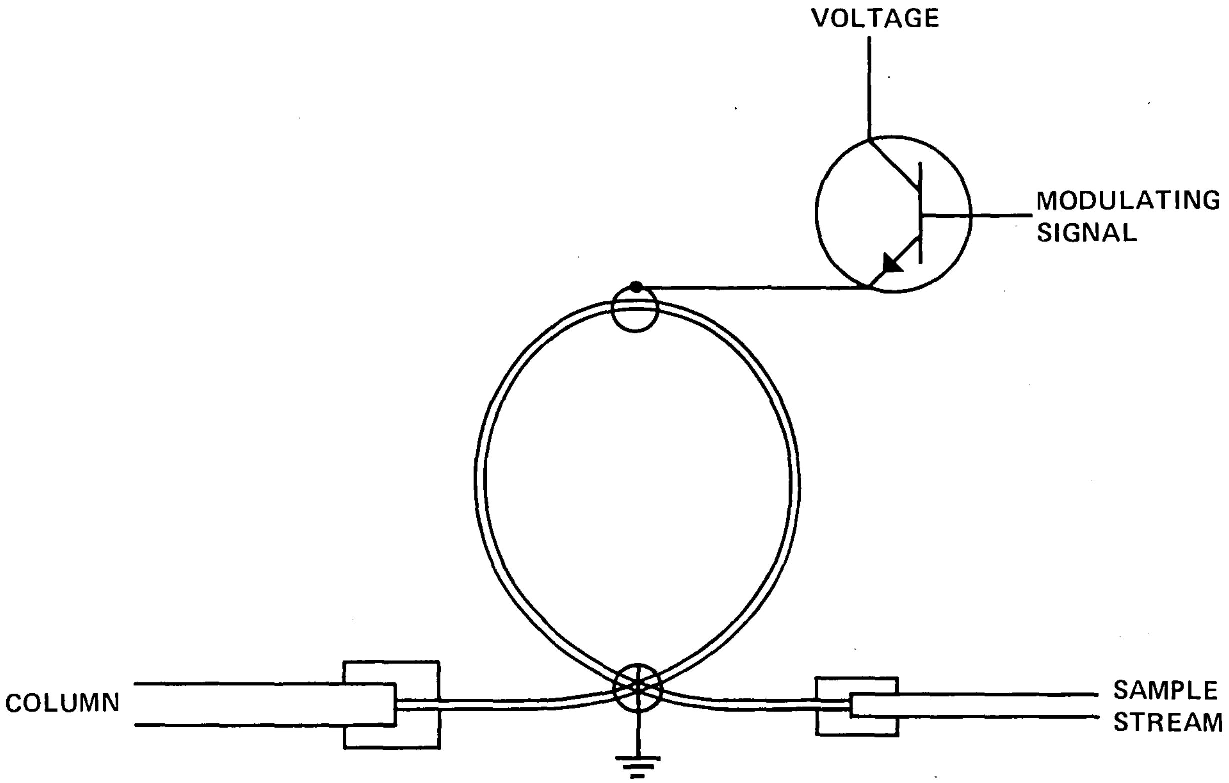

Figure 3

Diagram of a chemical concentration modulator for multiplex gas chromatography.

technique that lends itself particuarlay well to a selective modulation scheme. Selective modulation should have chromatographic applications analogous to selective detection.

Thermal Catalytic Modulator

Any chemical reaction which can be turned on and off rapidly and reproducibly in a flowing sample stream can form the basis of a modulator. Modulation is achieved by causing a chemical reaction to remove or otherwise modify the sample in the mixed stream prior to entry to the column. With this device, many types of reactions, both selective and non-selective, can be exploited, depending on the analytical need. Catalytic reactions are desirable so that the modulator itself is not changed or consumed during an experiment.

Goals

The main goals of this research were to determine the potential of multiplex chromatography, in combination with chemical modulators, for use in chemical analysis within space craft or other restricted environments and to develop several new multiplex techniques for use in specific applications. In order to achieve these goals, the equipment and computer software necessary to efficiently perform multiplex GC experiments in the laboratory were developed. Application of multiplex GC on board space craft is the eventual long term goal. Applications on Earth with similar instrumentation requirements, for example, real time analysis of trace organics in air sampled from an aircraft or in an open field, were also considered.

CHAPTER II

DESORPTION MODULATOR

This chapter describes the development of the thermal desorption modulator used in this part of this study (23). Examples showing the analysis of a complex mixture as well as an improvement in detection limits are presented.

Introduction

In multiplex gas chromatography (24), a sample enters the column over a relatively long period rather than as a single injection. The concentrations of the components of interest in the sample stream are modulated at the head of the column to give a chemical concentration signal which is dispersed by the column and observed at the detector. All previously reported examples used a valve to alternate between the sample and a reference stream and thus modulate the sample. However, other modulation techniques are also possible and may have important advantages in multiplex gas chromatography.

A simple and rugged chemical concentration modulator may be made by coating the inside wall of a narrow bore stainless steel tube with a GC stationary phase. A diagram of this modulator is shown and described in the section, Chemical Modulators, of Chapter I. A changing electrical current heats the walls of the tube by ohmic resistance changing the temperature of the tube and the stationary phase material within it. This changing temperature modulates the retention of some sample stream components in the tube to generate a chemical concentration signal in the flowing gas stream. No net sample dilution occurs because no additional reference or carrier gas is added. A previously described modulator for HPLC operates on the same principle except that the head of the column itself serves as the heated adsorbent (25). With a gas as the mobile phase, however, a larger signal is obtained if the adsorbent is placed within the heated tube because the heat capacity of the carrier gas is very low (26).

Experimental

Gas chromatographic experiments were done with a Carle (Anaheim, CA) model 111 GC equipped with a thermistor type thermal conductivity detector. The column was 1.5 m long by 1.1 mm ID packed with 3,4-dichlorophenyl isocyanate bound to Poracil C (100-200 mesh) (27). Samples composed of methane, ethane, propane, and butane (Matheson, Newark, CA) at various concentrations in ultra high purity helium (Matheson) were prepared. Additional samples containing the above substances plus isobutane, ethylene, acetylene, propene, propadiene, and propyne at various concentrations in helium were also prepared. The output signal was digitized by a Nelson Analytical (Sunnyvale, CA) model 700 analog-to-digital converter and transferred over an IEEE/488 bus to a PDP-11/34 computer (Digital Equipment, Maynard, MA) for calculations. The computational procedure has been discussed elsewhere (19) and briefly described in Chapter I.

The computer programs used in the data acquisition and in the calculations were written in Forth, version 1.3 (Forth Interest Group, San Carlos, CA) and are shown in appendices A, B, and C. Forth is a recently developed computer language which allows programmers to define words that perform a described operation. The theory of Forth is based on a hierarchy of definitions, "words", where new definitions are a combination of words previously defined. A new word, once defined and tested, is immediately ready for use and becomes an integral part of the language. The program used in plotting the chromatograms was written in Fortran IV, version 2.6 (Digital Equipment Corp.) and is shown in appendix D.

The first modulator tube was 0.381 mm OD by 0.254 mm ID by 10 cm long 304 stainless steel. It was coated by passing 5 mL of 20% SF-96 (General Electric, Silicon Products Dept., Waterford, NY) in dichloromethane (Eastman Kodak Co., Rochester, NY) through the tube at 10 psi pressure at room temperature. A second modulator was prepared similarly but coated with 5 ml of 20% OV-101 (Applied Science Lab., Inc., State College, PA) in dichloromethane through the tube at 1 psi pressure at room temperature. A third modulator was prepared from a stainless steel tube of much larger length, 112 cm, and coated with 10 ml of 50% OV-101 in dichloromethane at 10 psi pressure at room temperature.

Results and Discussion

Figure 4 is a chromatograph obtained using a conventional 0.1 mL injection as the modulation signal. The four peaks are due to methane, ethane, propane, and butane at 10 ppm. The noise is predominantly from the detector and its associated electronics and results in a detection limit of about 10 ppm.

Figure 5 is the chromatogram obtained from a single current pulse using SF-96 as the stationary phase in modulator number 1. The three peaks, due to ethane, propane, and butane at 1000 ppm, each consist of

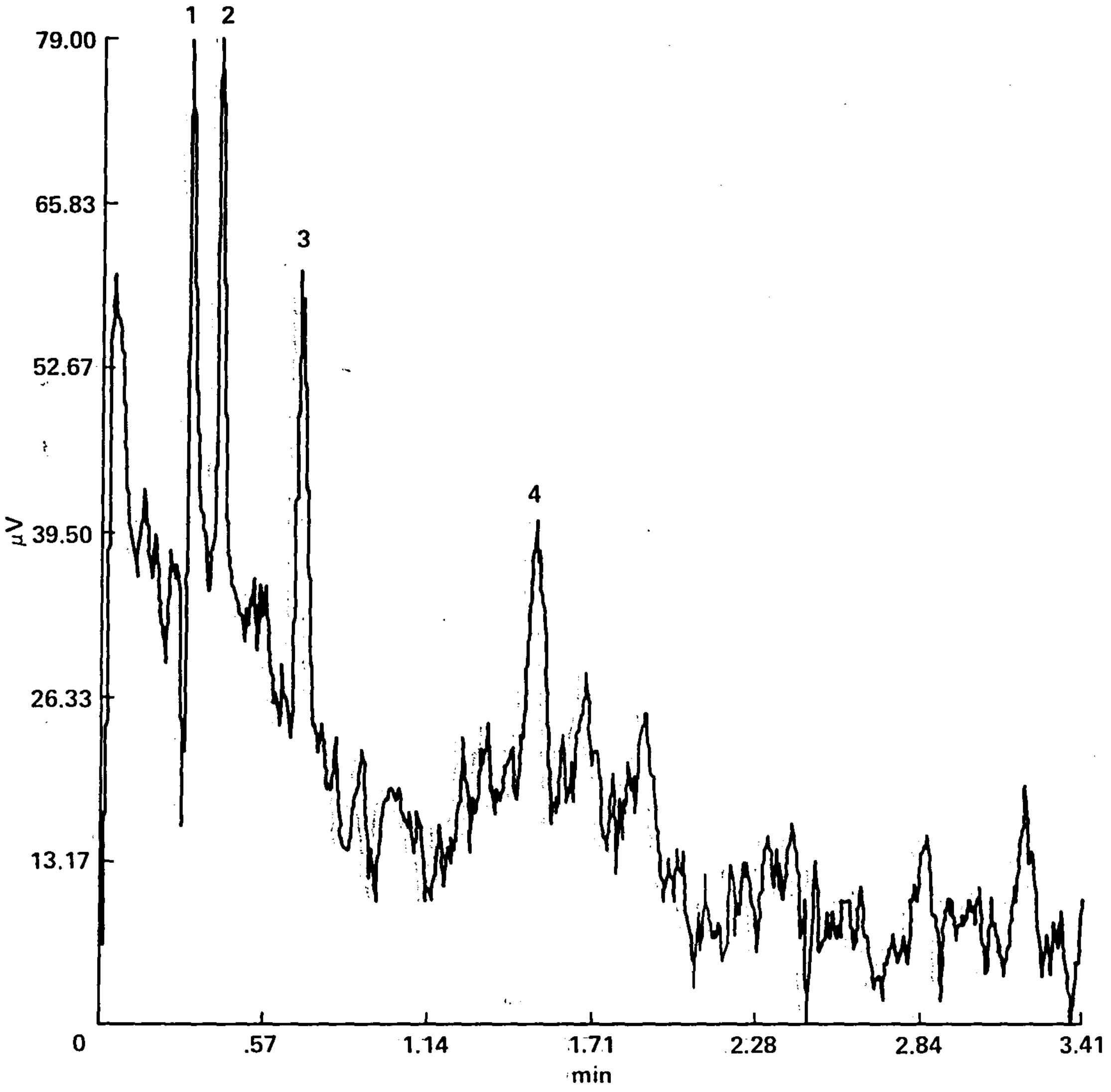

Figure 4

Chromatogram obtained using a conventional 0.1 mL injection with a rotary valve. The four peaks correspond to 1. methane, 2. ethane, 3. propane, and 4. butane. The detection limit using this conventional GC sampling is about 10 ppm.

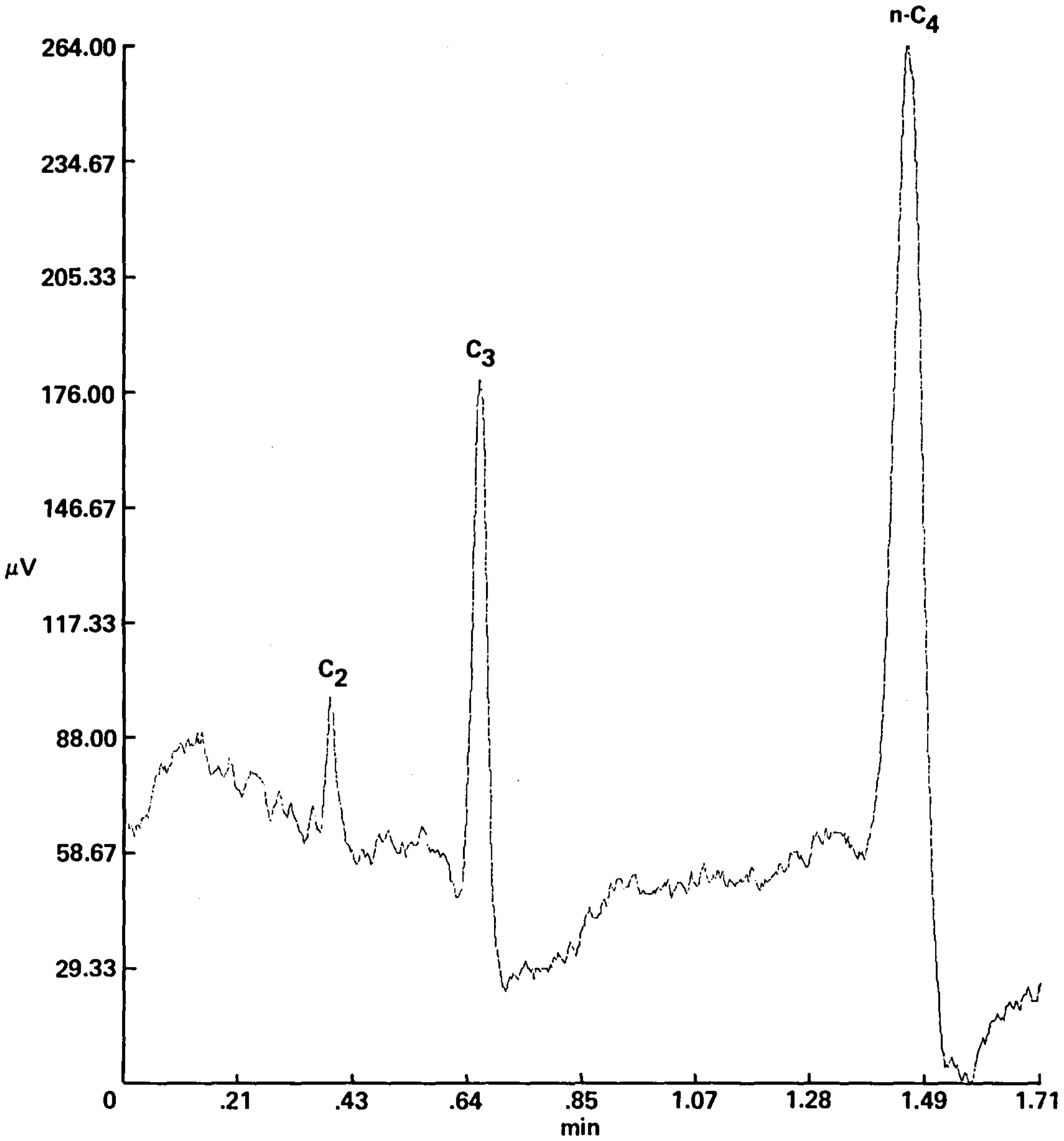

Figure 5

Chromatogram obtained from a single 6 watt current pulse for 0.6 second using SF-96 modulator stationary phase. The three peaks correspond to ethane, propane, and butane at 1000 ppm.

a positive part corresponding to sample released upon heating and a negative part corresponding to sample sorption as the coating cools. The differences in peak intensities are due to differences in retention of each component in the SF-96 coating. No peak is seen for methane because it is not retained by the SF-96 stationary phase at room temperature. The positive part of each peak is sharp because all of the sample is released from the stationary phase suddenly when it is heated and moves at the carrier gas velocity on to the column. The negative part of each peak is broad because the modulator is cooled as fresh sample flows into it to refill the stationary phase. Sample is retained in the cool stationary phase and moves slowly through the modulator.

Figure 6 is the chromatogram obtained by cross-correlation for the four component mixture at 100 ppm using the SF-96 coating in modulator number 1. Some of the noise is correlation noise caused by an approximation in the computation. This could be eliminated by a more sophisticated procedure but, in any case, is reduced in proportion to the analytical signal. The remaining noise is predominantly from the detector and electronics and results in a detection limit of about 10 ppm which is comparable to the detection limit for a conventional single injection chromatogram using the same column and detector. The limiting factor is the amplitude of the chemical concentration signal generated by this modulator.

Figure 7 is a chromatogram obtained by a similar experiment for the ten component mixture at the concentrations given in the figure using modulator number 2. The 8 substances listed in the figure are the ones effectively modulated by this modulator. Methane is not

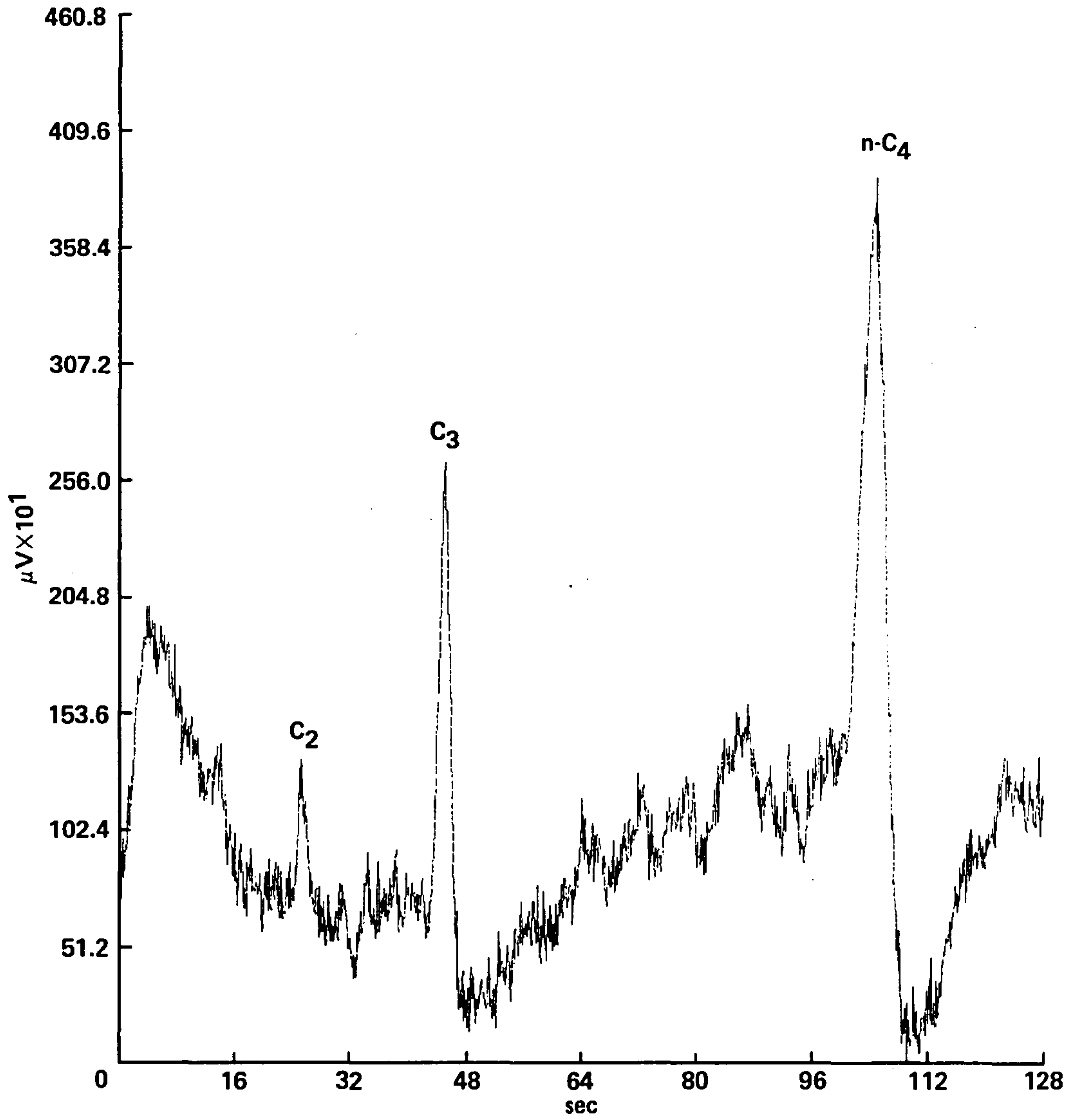

Figure 6

Chromatogram resulting from cross-correlation of pseudo-random modulation signal with detector output signal using SF-96 coated modulator. The modulation signal was a series of 6 watt current pulses applied for 0.1 second each with an average duty cycle 0.035. A total of 3166 pulses were generated during a 264 min determination. The three peaks correspond to ethane, propane, and butane. The detection limit of about 10 ppm is comparable to that obtained using conventional methods.

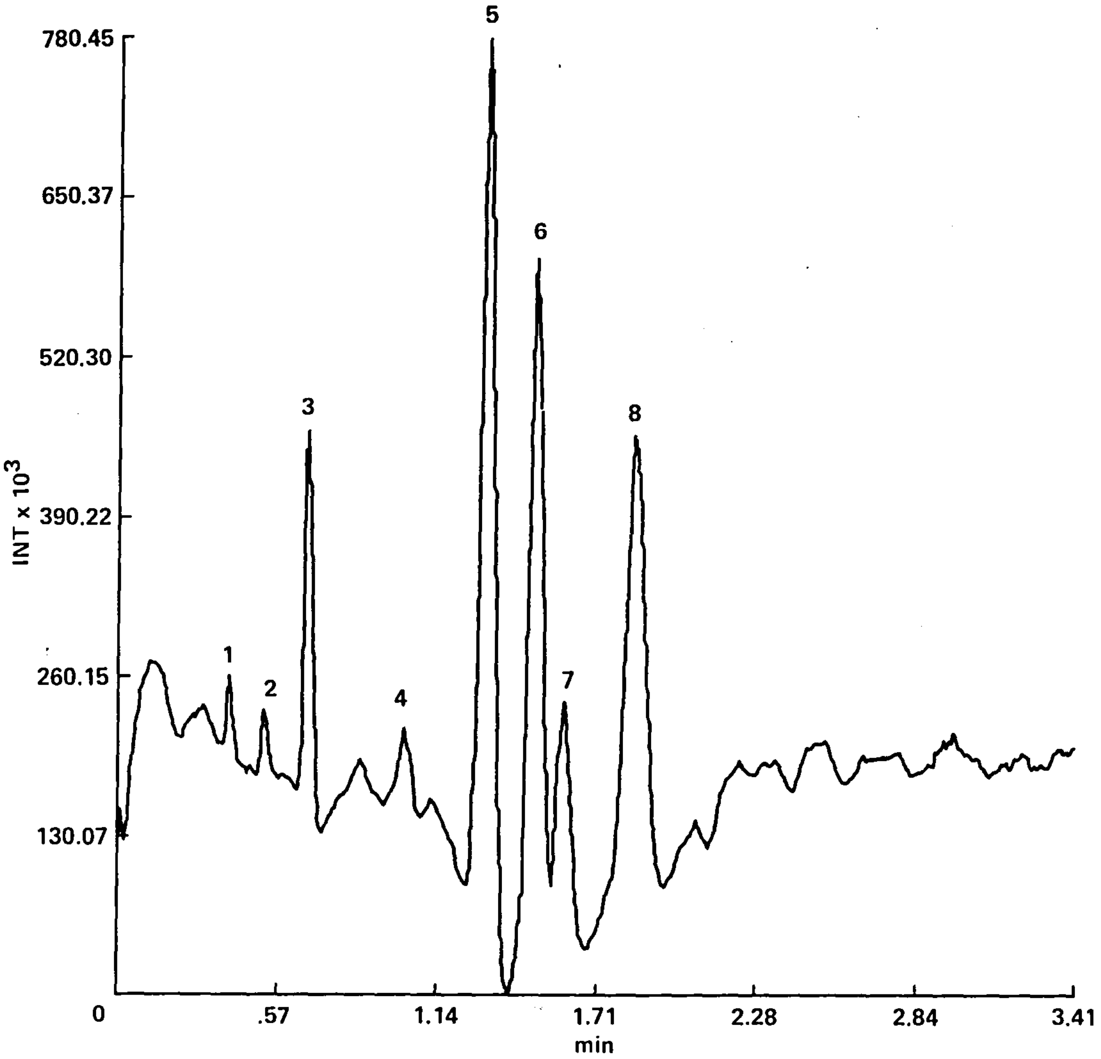

Figure 7

Chromatogram obtained from cross-correlation of pseudo-random modulation signal with detector output signal for the ten component mixture using the OV-101 coated modulator. Sample mixture contains 1. ethane (31 ppm), 2. ethylene (63 ppm), 3. propane (63 ppm), 4. acetylene (94 ppm), 5. isobutane (94 ppm), 6. butane (125 ppm), 7. propene (125 ppm), 8. propadiene (156 ppm). The modulation signal was a series of 6 watt current pulses applies for .4 seconds each with an average duty cycle of 0.027. A total of 1058 pulses were generated during a 307 min determination.

modulated because of its low affinity for this coating material. Propyne is poorly modulated because it is strongly retained on the column and appears as a very low, broad peak beyond the end of the chromatogram.

Figure 8 is the chromatogram obtained by cross-correlation for the four component mixture at 0.1 ppm using the OV-101 as the stationary phase in modulator number 3. The two peaks are due to propane and butane, respectively. A 100-fold improvement in sensitivity and detection limit over what is possible by conventional GC is obtained. No peaks are seen for methane and ethane because of their low affinity for this adsorption material. The large peak at short retention times is probably due to a carrier gas flow disturbance caused by expansion of the gas within the heated modulator.

A simple chemical modulator based on thermal desorption from standard GC stationary phases works well as a chemical signal generator for multiplex GC by modulating most or all components of the sample. Those components that are not retained in the stationary phase are not modulated and remain part of the gas stream. The modulation efficiency of those that are modulated depends on the adsorbent capacity of the components. The adsorbent capacity may vary widely for different components of a sample stream and may also depend on operational factors such as heating rate and modulator length. At higher temperatures, sample substances are retained less and migrate through the modulator column faster than at low temperatures. The length of the modulator directly affects both the degree of modulation through the amount of sample retained within it and the maximum possible modulation frequency through the time required for sample to

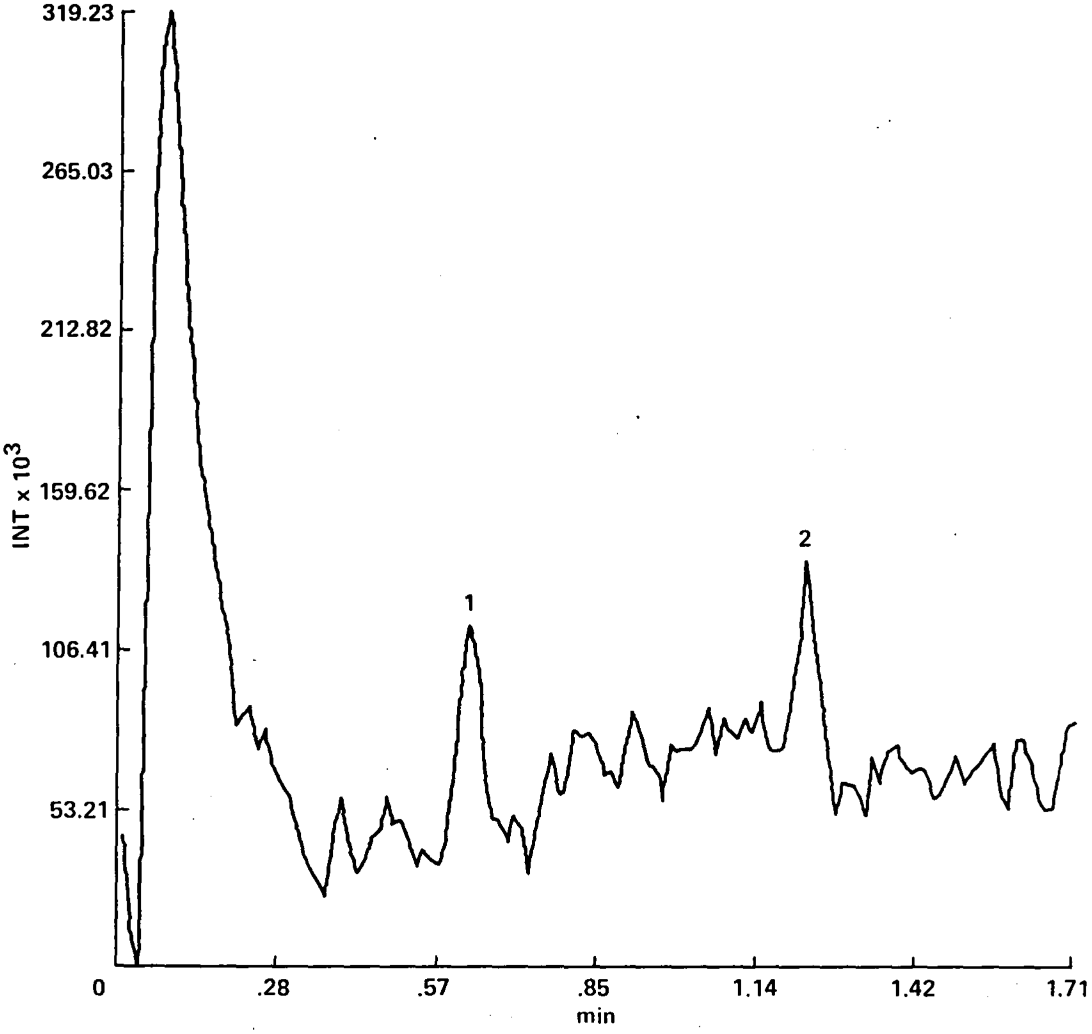

Figure 8

Chromatogram resulting from cross-correlation using the long OV-101 coated modulator. Sample mixture contains methane, ethane, propane, and butane at 0.1 ppm. The modulation signal was a series of 14 watt current pulses applied for 0.8 seconds each with an average duty cycle of 0.027. A total of 270 pulses were applied during a 154 min determination.

elute through it. A longer modulator gives a higher degree of modulation but at a lower frequency.

Thermal desorption modulators maximize throughput since sample is neither destroyed nor diluted. These modulators impose a chemical concentration signal on the sample stream, but do not change the average concentration.

There is no need to wait for very slowly eluting substances, like propyne to elute before additional samples can be added. Therefore, propyne can be ignored in the cross-correlation calculations and it will not interfere with the determination of other components present.

An improvement in detection limits predicted for multiplex chromatography, has been achieved using this type of modulator. A simple and inexpensive thermal conductivity detector can be made to perform as well as more sophisticated detectors like the flame ionization detector.

CHAPTER III

DECOMPOSITION MODULATOR

This chapter describes concentration modulation by thermal decomposition for multiplex gas chromatography (28). Thermal decomposition is a simple example of a selective modulator.

Introduction

In multiplex gas chromatography a large sample volume enters the column over a long period of time as a pseudo-random sequence of concentration pulses. The chromatogram is then recovered by computational deconvolution of the resulting signal (24). Several types of devices have been constructed which modulate the sample stream producing multiple concentration pulses (19,20,21,22,23). These devices modulate most or all components of the sample mixture. Devices which modulate the concentration of specific sample molecules or classes of molecules can provide additional analytical selectivity useful with, for example, very complex sample mixtures. Selective modulation should have applications analogous to selective detection. Thermal decomposition is a simple technique that lends itself particularly well to a selective modulation scheme. Modulation of a GC sample stream using thermal decomposition has previously been used by Lovelock between the column and the detector to improve detection limits and eliminate baseline drift (29).

In the technique reported here, thermal decomposition is used at the inlet of the column to create concentration pulses in a continuously flowing sample for analysis by multiplex gas chromatography.

Since application of a pulse to the thermal decomposition modulator removes substances from the sample stream, the resulting chromatogram contains vacancies rather than peaks and is similar to vacancy chromatography in which a pure carrier gas pulse is injected into a continuously flowing sample stream (30).

Experimental

The study was conducted with a Carle AGC Model 111 gas chromatograph equipped with a thermistor bead detector and an external sample modulator system described previously in Chapter II. The system reported here differs from the previous one in that a 0.25 mm ID by 0.38 mm OD by 21.6 cm long uncoated 304 stainless steel capillary tube was used as the modulator. Electric power pulses at 250 watts were applied to the capillary tube modulator as directed by the pseudo-random modulation signal. For Figure 9, the data acquisition time was 0.4 s. A total of 459 pulses, 0.4 s long, were generated during a 137 min determination for an average duty cycle of 0.0233. For Figure 10 the data acquisition time was 0.8 s. A total of 345 pulses 0.8 s long were generated during a 154 min. determination for an average duty cycle of 0.0299. Following each pulse, there was a minimum 2.4 s dead time during which no additional pulses occurred allowing the modulator to cool and return to its initial condition. Except during this dead time, the probability of a pulse was 0.036. Samples were prepared by blending mixtures of various concentrations of hydrocarbons in helium with ultra high purity helium using a Brooks Emerson dual channel mass flow controller (Hatfield, PA). The ultra high purity helium was pretreated prior to

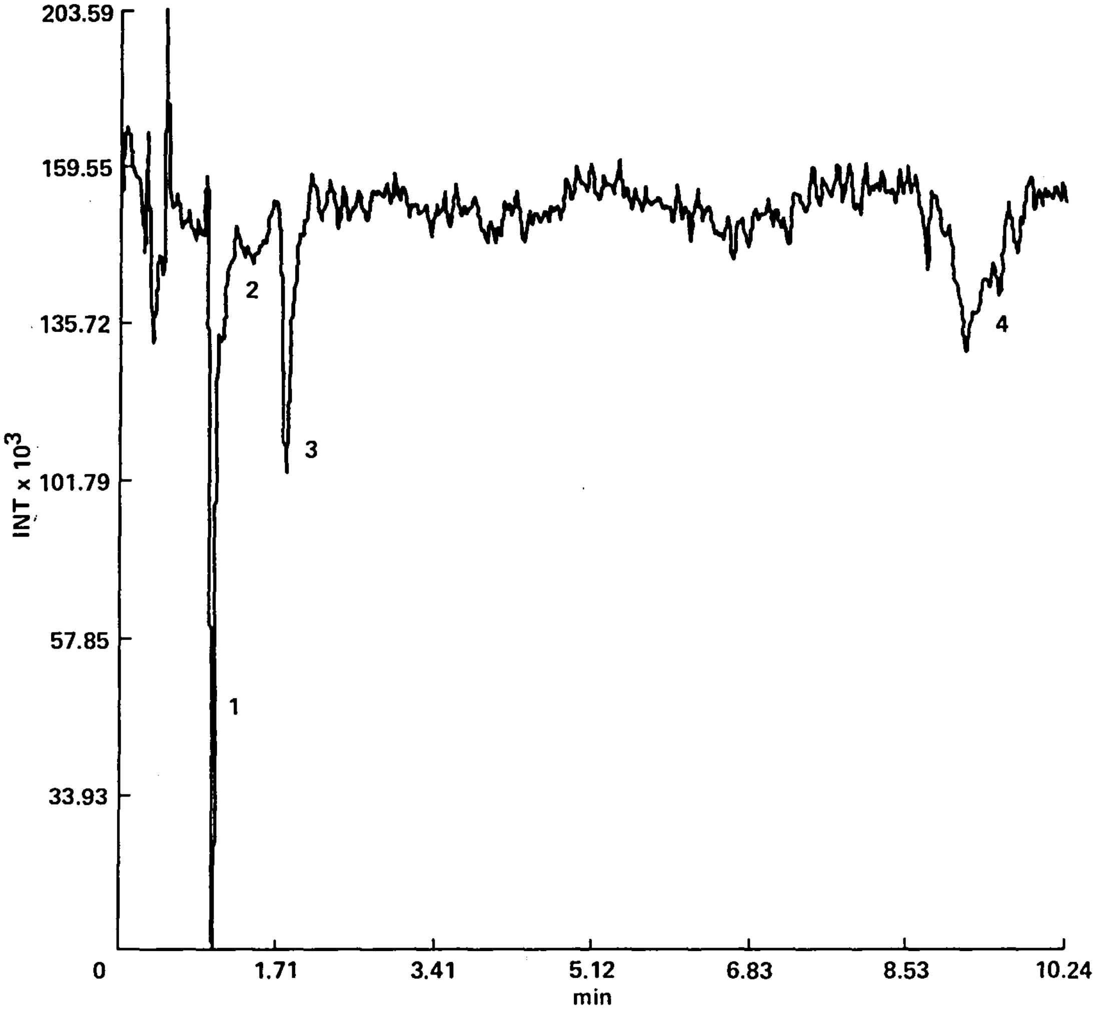

Figure 9

Vacancy chromatogram resulting from cross-correlation of pseudorandom modulation signal with detector output signal. Sample mixture contains methane (31 ppm), ethane (31 ppm), propane (63 ppm), butane (63 ppm), isobutane (94 ppm), ethylene (94 ppm), acetylene (125 ppm), propene (125 ppm), propadiene (156 ppm), and propyne (156 ppm). Vacancy peaks correspond to 1. acetylene, 2. propene, 3. propadiene, 4. propyne. GC column temperature = 25 C. Flow rate = 14.0 sccm. The column was 1.5 m long by 1.1 mm ID packed with 3,4-dichlorophenyl isocyanate bound to Poracil C (100-200 mesh) (27).

blending by passing it through a 1.1 mm ID by 1.6 mm OD by 66 cm long 304 stainless steel tube mounted in a furnace at 700 C in order to eliminate any contaminant that could be modulated by thermal decomposition. The blended sample flow rate was 14.0 scc/min. The computaonal procedure was the same as previously described in chapter I.

Results and Discussion

Figure 9, which illustrates selective modulation, is the computationally recovered vacancy chromatogram of a mixture of ten hydrocarbons. Only those unsaturated hydrocarbons unstable at the temperatures reached by the modulator are decomposed and removed from the sample stream resulting in vacancy responses. Figure 10, which illustrates the sensitivity achieved with thermal decomposition modulation, is a similar chromatogram obtained from a sample mixture where the concentrations have been reduced by a factor of 1000. Both acetylene and propadiene at 0.1 ppm represent a 100 fold improvement in detection limit for thermal decomposition multiplex gas chromagraphy over a conventional, 100 1 single injection determination using the same column and detector. The same improvements can be expected for other similar applications of multiplex gas chromatography.

A vacancy followed by a sharp positive peak, was observed at short retention time. These appear to be caused by trace impurities in the sample mixture. The vacancy correspnds in retention time to carbon monoxide and the sharp peak to carbon dioxide. When the modulator is hot, carbon monoxide impurity reacts on the metal surface to give carbon dioxide and carbon.

$$200 = C + CO_2$$

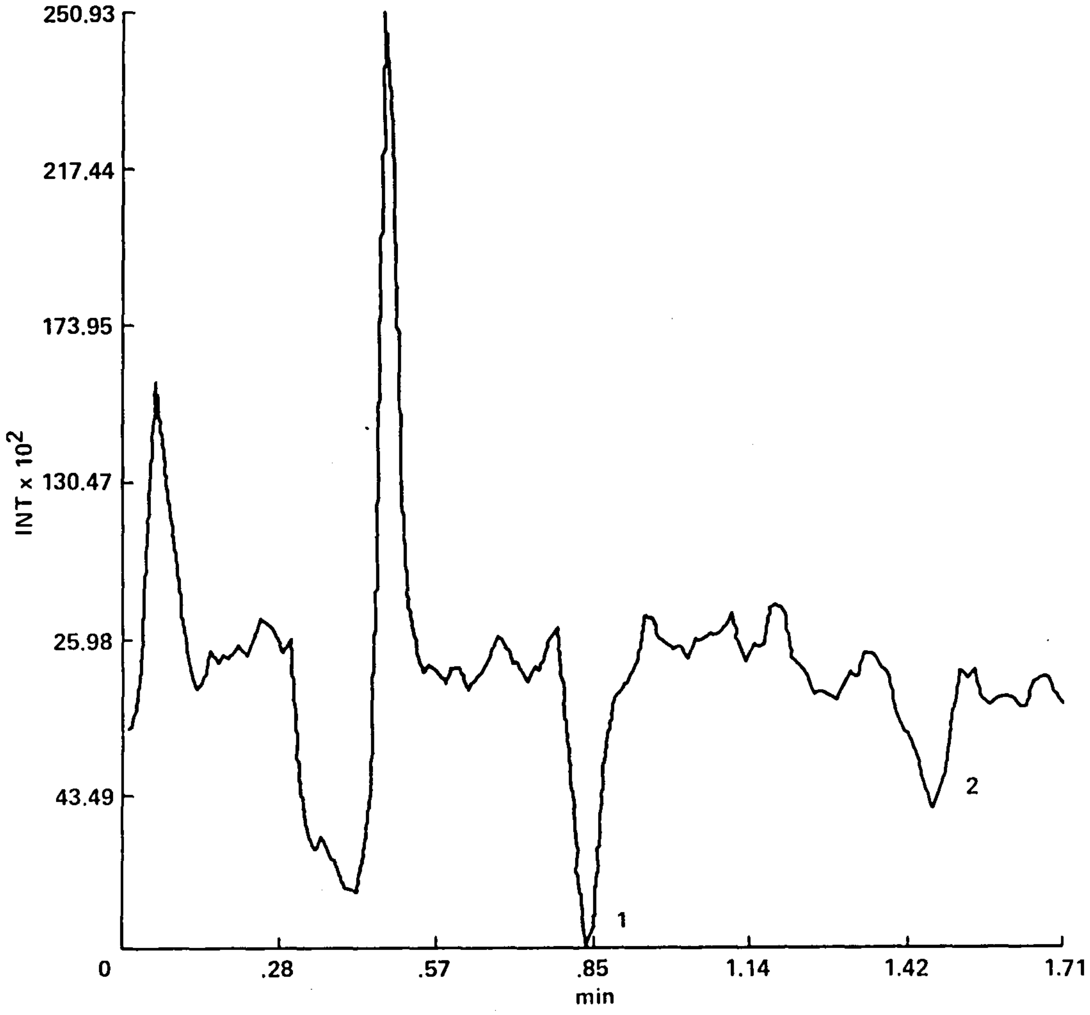

Figure 10

Vacancy chromatogram resulting from cross-correlation. Same mixture as in Figure 9 except the concentrations have been reduced by a factor of 1000. Vacancy peaks correspond to 1. acetylene (0.1 ppm), and 2. propadiene (0.1 ppm). The vacancy and peak preceding vacancies 1 and 2 correspond to carbon monoxide and carbon dioxide respectively. GC column temperature = 35 C. Flow rate = 14.0 sccm.

This reaction is known to occur on hot metal surfaces (31). The carbon dioxide is eluted as a positive product peak while the removal of carbon monoxide results in a vacancy immediately preceding it.

The concentration of carbon monoxide in the sample is not known. But, if the heated tube in the ultra high purity helium stream used for sample dilution is removed, then the vacancy and peak become much larger. Most, if not all, of the carbon monoxide is probably from the original sample mixture which, of course, could not be pretreated at high temperature. The sample stream in this experiment contained only 3.6% of the untreated sample mixture. If we assume that all of the carbon monoxide came from the untreated standard and the carbon monoxide concentration in this ultra high purity helium is a typical 2 ppm, then the peak and vacancy correspond to 70 ppb of carbon monoxide. This is of the same order of magnitude as the concentrations of the other sample stream components and would be expected to give a signal of similar size.

This chapter has demonstrated selective modulation in the analysis of a complex mixture. The improvement in detection limit and sensitivity is comparable to that obtained by thermal desorption modulation. Thermal decomposition is only the simplest example of a chemical reaction used for selective modulation. Many other kinds of reactions are potentially useful as modulators for multiplex gas chromatography. For example, the carbon monoxide reaction accidentally discovered here might be used to measure carbon monoxide.

Selective modulators are potentially just as useful as selective detectors in gas chromatography. Selective modulators have an advantage over selective detectors, however, in that it is much easier to implement a given chemistry for a modulator than it is for a detector. In Chapter IV a catalytic type of modulation is applied for the analysis of an environmental sample using multiplex methods.

CHAPTER IV

DETERMINATION OF METHANE IN AMBIENT AIR BY MULTIPLEX GAS CHROMATOGRAPHY USING A THERMAL CATALYTIC MODULATOR

This chapter describes a practical application of multiplex chromatography using a catalytic modulator to monitor methane in ambient air (32). This is another example of a selective modulator.

Introduction

Methane is of interest in the study of Earth's atmosphere because of its implication in the possible future global warming of the Earth's surface (33,34). This warming or "greenhouse effect" is produced by the absorption of infrared energy by trace gases (35). Methane has been of particular interest because it has both natural and anthropogenic sources. Ehhalt and Schmidt (36) have estimated that between 10 and 30% of the annual global production of methane is from enteric fermentation associated with animals, mostly cattle; 25 to 45% is emitted from rice paddy fields; and only 2 to 5% is produced directly from anthropogenic activities such as industrial processes, coal and lignite mining, fuel oil production, and automobile exhaust. Increases in these methane emissions have been linked to growth in the human population (37,38). It has been estimated that in the next 40 to 50 years, methane could contribute 20 to 25% as much atmospheric warming as that expected from carbon dioxide increases (35,39).

With the expected increase in atmospheric methane, it will be important to accurately monitor the concentration over long and contiguous periods of time. Therefore, studies to investigate sources, sinks, and cycles of methane will require analytical methods capable of continuous unattended measurement with temporal resolution of an hour or less for weeks at a time. Various experimental techniques have been used for the measurement of methane in ambient air in addition to other constituents in the earth atmosphere. Smith (40) compiled atmospheric gas concentration profiles from 0 to 50 km by IR absorption spectroscopy. Dianov-Klokov et al. (41) monitored variations of methane abundance in the atmosphere using the method of absorption spectroscopy with the sun as the light source and found seasonal variations in the concentration of methane.

Gas chromatography has proven to be one of the most powerful tools available for the determination of trace amounts of organic substances in air (37). Although gas chromatography has been widely used in trace atmospheric analysis, conventional gas chromatography has some serious limitations. First, detector sensitivity is constrained by the sample volume limitations of the column. Only relatively small volumes of sample may be introduced into the column and then these samples are further diluted by the carrier gas during the chromatographic process. Therefore, in order to make trace-level measurements, sensitive and usually sophisticated detectors must be employed. Second, only discrete sample injections, widely separated in time, may be introduced since all sample components must elute before a subsequent analysis may begin. Thus, only slowing changing systems may be monitored. Finally, a consumable carrier gas is usually required even when the sample itself is a gas. This requirement limits the usefulness of the conventional gas chromatograph in long term unattended operation. Multiplex gas chromatography provides an alternative method to deal with these limitations (24).

In multiplex gas chromatography, there is no need to wait for a chromatogram to be completed before inputting additional samples. A new sampling cycle may begin as often as every few seconds. This effectively increases the sample throughput by a large factor and leads to two important advantages. First, a number of samples in a short period may be treated statistically to increase the signal to noise ratio and confidence in the measurement (the technique exploited in this work). Second, many discrete chromatographs may be acquired in a short time. However, the chromatograph must be under computer control, and the final chromatogram can only be obtained computationally by applying deconvolution techniques such as cross-correlation to the detector output signal.

Multiplex gas chromatography, like conventional chromatography, requires that the carrier stream be modulated in terms of sample concentration and various devices, both mechanical and chemical, have been developed to meet these requirements (20,21,22,23,28,26). These modulation devices must generate reproducible and frequent chemical concentration pulses or changes in the carrier stream. Mechanical devices create the modulation signal by switching between the carrier gas stream and a sample stream as often as several times a second. Chemical devices require that the sample be uniformly mixed into the carrier gas or that the sample stream itself serve as the carrier. Modulation is achieved by causing a chemical reaction to remove or otherwise modify the sample in the mixed stream prior to entry to the column. This is accomplished, as for example in this study, by applying continuous electrical heating to a short length of tubing containing a reactive bed. The tube or modulator is then periodically cooled for short time intervals either by interrupting the current or by introducing some form of forced cooling. With this device, many types of reactions, both selective and non-selective, can be exploited, depending on the analytical need.

The objective of the work reported here was to develop an effective and accurate gas chromatographic method to monitor local variations in concentration of methane in the atmosphere over long periods of time using a very modest gas chromatograph with no requirement for consumables beyond power. The technique developed uses a rudimentary, commercial gas chromatograph modified for multiplex chromatography by the addition of a chemical modulator. This technique, with modifications, should be applicable to the monitoring of many other trace components in air as well as some process gas streams.

Experimental

The chromatographic system developed for this work is shown in Figure 11. The central component was a model 1000 Bio-Gas Chromatograph (Okemos, MI) equipped with a Tin Metal Oxide semiconductor detector and a 1/8-inch O.D. X 0.028-inch wall X 7-feet long stainless steel column packed with 80-100 mesh Alcoa Type F-1 Alumina (Matheson Coleman and Bell). The detector in this instrument operates by catalytically oxidizing hydrocarbons in the presence of air and measuring the heat released. The modulator was prepared from 1/16-inch O.D. X 0.010 inch wall X 4 1/2-inch long 304 stainless steel tube

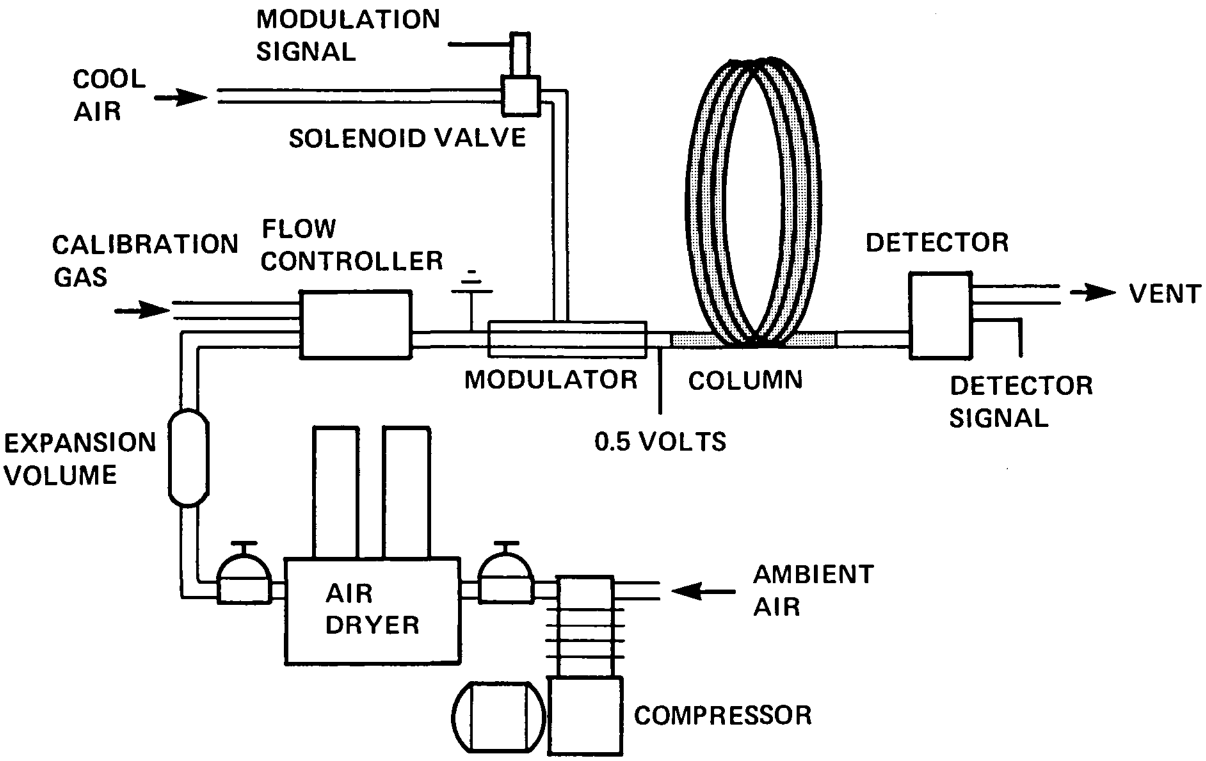

Figure 11

Schematic showing the major components of the chromatographic system for the determination of methane in ambient air.

loosely packed with 9.80 mg of Silver(I) Oxide powder (General Chemical Division of Allied Chemical). This tube was fitted with a jacket through which a pulse of cool compressed air could be introduced upon command. The modulator was attached directly to the head of the column and to one output channel of a model 5841 Brooks Emerson Dual Channel Mass Flow Controller (Hatfield, PA) which controlled the flow at 14.0 scc/min. The air to be analyzed was supplied to the flow controller from a model HF 300-106-012 Puregas Heatless Air Dryer (General Cable Corp., Apparatus Division, Westminster, CO) to which a 1.0 L expansion volume and pressure regulator were added to minimize pressure pulses. The dryer removed water and any high molecular weight contaminants from the ambient air without affecting the methane concentration. Ambient air at a regulated pressure of 25 psig was supplied to the dryer by a model LC Bell and Gossett ITT Oil-less Air Compressor (Morton Grove, IL). The system was operated as previously reported multiplex chromatograph systems (23,28) and in Chapters II and III, using a Digital Equipment Corporation PDP 11/34A computer through a IEEE 488 interface attached to a model 760 Nelson Analytical A/D Interface both providing the modulation signal and acquiring the detector signal. The modulator was continuously heated to slightly below the decomposition temperature of silver oxide by applying 0.5V(3.6w) directly to the ends of the stainless steel tubing. This modulator was maintained hot in order to remove methane from the previously treated ambient air. Modulation was accomplished by periodically cooling the bed with an external stream of compressed air thus momentarily allowing methane in the air carrier to reach the column. A modulation pulse, generated by the computer, opened a valve allowing compressed air at 90 psig to flow at 2 liters/min. through the surrounding jacket thus cooling the silver oixide bed sufficiently to allow methane to enter the column. Each pulse was 0.4 seconds in length and constrained not to occur again for at least 0.8 seconds. Except for this "dead" time, the probability of a pulse was 0.027. Acquisition cycle times were 30.7 minutes with 105 pulses for the calibration experiments, and 61.4 minutes with 224 pulses for the eight day experiment. For these experiments, the same modulation signal was repeated for each data set within that experiment. The acquisition procedure used to control the chromatographic system and the computational procedures used to obtain the chromatograms have been reported elsewhere (23,28,26,25) and in Chapters II and III.

Calibrations of the system were conducted using the standard addition method. Mixtures containing various concentrations of methane in air (Air Products, Allentown, PA) were prepared manometrically and introduced into the analytical stream using the second channel of the flow controller.

To test the sensitivity of the system toward carbon monoxide, which is also present in pretreated air, similarly prepared mixtures containing various concentrations of carbon monoxide in ambient air were also introduced into the system and run under the same experimental conditions.

Results and Discussion

A multiplex gas chromatographic technique, using an instrument with modest components, was developed which was capable of monitoring methane concentrations in ambient air over extended periods.

Multiplex chromatography has been previously proposed for trace analysis of complex samples (20) and the usefulness of correlation techniques for the analysis of prepared methane samples in air using helium as a carrier gas and a flame ionization detector has been reported (42). The use of multiplex gas chromatography in the analysis of a real environmental sample is, however, reported here for the first time.

One of the expected problems in the analysis of any real sample by any method is interferences and complications caused by matrix effects. These are often both unknown and variable and, in some cases, can be so complex that it is impractical to define them all. Chromatography can usually reduce matrix problems significantly through partial or complete resolution of the components of interest and, if appropriate, through use of a detector sensitive to only certain classes of molecules. Multiplex gas chromatography can provide these same benefits; in addition it offers some unique benefits not attainable with the conventional techniques.

The elimination of the need for a separate carrier gas is one such benefit realized here. Because multiplex gas chromatography makes use of a high volume sample throughput and because the specialized detector used here requires significant concentrations of oxygen, a separate carrier gas is not needed. Air has previously been used as a carrier in gas chromatography to study the effect of on-column oxidation on the efficiency of apolar stationary phases (43). It has also been used as a carrier gas in a portable gas chromatograph (44). With ambient air, which is relatively homogeneous in terms of sample to be analyzed, serving as both sample and carrier, some means must be provided to introduce concentration pulses in the gas stream. Mechanical valves which alternate between the sample and reference stream to produce the desired modulation (20,21,22) were unacceptable in this work because of the need for a consumable reference gas stream. Chemical devices have been reported, in Chapters I and II, that modulate the sample concentration in a mixed gas stream. These include a thermal decomposition modulator which removes some components of the mixed stream upon heating (28) and two thermal desorption modulators which selectively desorb compounds either from the head of the column (26) or from a small precolumn coated with stationary phase (23) upon heating. However, the decomposition modulator was ineffective for methane and the thermal desorption devices were susceptible to degradation, unable to absorb the light gases efficiently, or produced unacceptable flow variations during the modulation cycle. Therefore, a new chemical modulator based on thermal reactions with silver oxide was developed.

Silver oxide has previously been used for the removal of trace amounts of hydrocarbons from helium and air carrier gas streams by oxidation to water and carbon dioxide on a bed at 200 C eventually consuming the silver oxide (45). By use of high ratios of oxygen to methane at high pressure, a silver oxide bed at 375 C has been found to catalytically oxidize methane to formaldehyde and methanol (46). Silver oxide at elevated temperature has also been found to catalytically oxidize methane to various products including ethylene and ethylene oxide (47). A small heated bed of silver oxide was found in this work to catalytically react with the methane in ambient air at 12 psig. The products of this reaction have not been determined, however, methane is consumed and no product attributable to methane was detectable with the oxidative detector.

The efficiency of this modulation is low at these operating conditions (estimated to be about 1%), but sufficient signal is produced to readily allow quantitative determinations of ambient methane concentrations. During a modulation pulse or cycle, the concentration of a modulated substance is not required to alternate between zero and 100% of its initial concentration, but it must be reproducible and should be directly proportional to the total concentration. The DC level of the modulation and the proportionality constant relating modulation to total concentration are not critical beyond sensitivity and dynamic range considerations. Other modulators packed with cobalt, copper and manganese oxides were also tested and some modulation was observed. Silver oxide was found to have the highest modulation efficiency and reproducibility for carbon monoxide and only 1.0 ppm for methane. In this application, the detector has enough sensitivity so that even an inefficient modulator gives an adequate signal.

Significant reaction with other higher molecular weight hydrocarbons was observed. These components produced severe baseline drift from the continued introduction of slowly eluting species and rapidly drove the detector into saturation. This problem was solved by the addition of a dryer which removed all but the noble gases, nitrogen, oxygen, hydrogen, carbon monoxide, carbon dioxide, and methane. The remaining baseline drift, attributed to the minor thermal and electronic instabilities, was easily corrected by subtracting a 200 point moving average from each data point during acquisition.

The instrument was found not to detect carbon monoxide in these experiments. Carbon monoxide is, however, oxidizable and was not removed from the sample stream. Further, carbon monoxide in ambient air can be found in concentrations of 0.04 ppm to 0.5 ppm in unpolluted areas (48) and up to 13 ppm in very polluted ones (49,50). Since the detector has a detection limit of 0.1 ppm for carbon monoxide and only 1.0 ppm for methane for a 1cc conventional GC injection, carbon monoxide should have been detectable if modulated. Therefore, a series of experiments were run to test the efficiency of the modulator towards carbon monoxide. Using calibration standards prepared in air, the modulator was found to be 400 times more efficient for methane than for carbon monoxide. Stevens et al. (48) have taken advantage of the selectivity of the Schultze reagent (I_2O_5) to selectively oxidize the carbon monoxide in ambient air in the presence of methane. A modulator specifically for carbon monoxide could be designed based on that reaction.

Figure 12 is the calibration curve obtained for the system by the standard additions method. The experimental data for this calibration curve are shown in Table I. Various concentrations of methane in compressed air were added to the ambient air stream after the stream had passed through the dryer. It would have been better to mix the standard with ambient air before passing the stream through the dryer, but this was impractical because the dryer requires in excess of 100 L/minute flow rates and no practical method was available to prepare such large volume standards. The compressed air standards added contaminants normally removed from the ambient air samples and raised the background noise level of the calibration chromatograms.

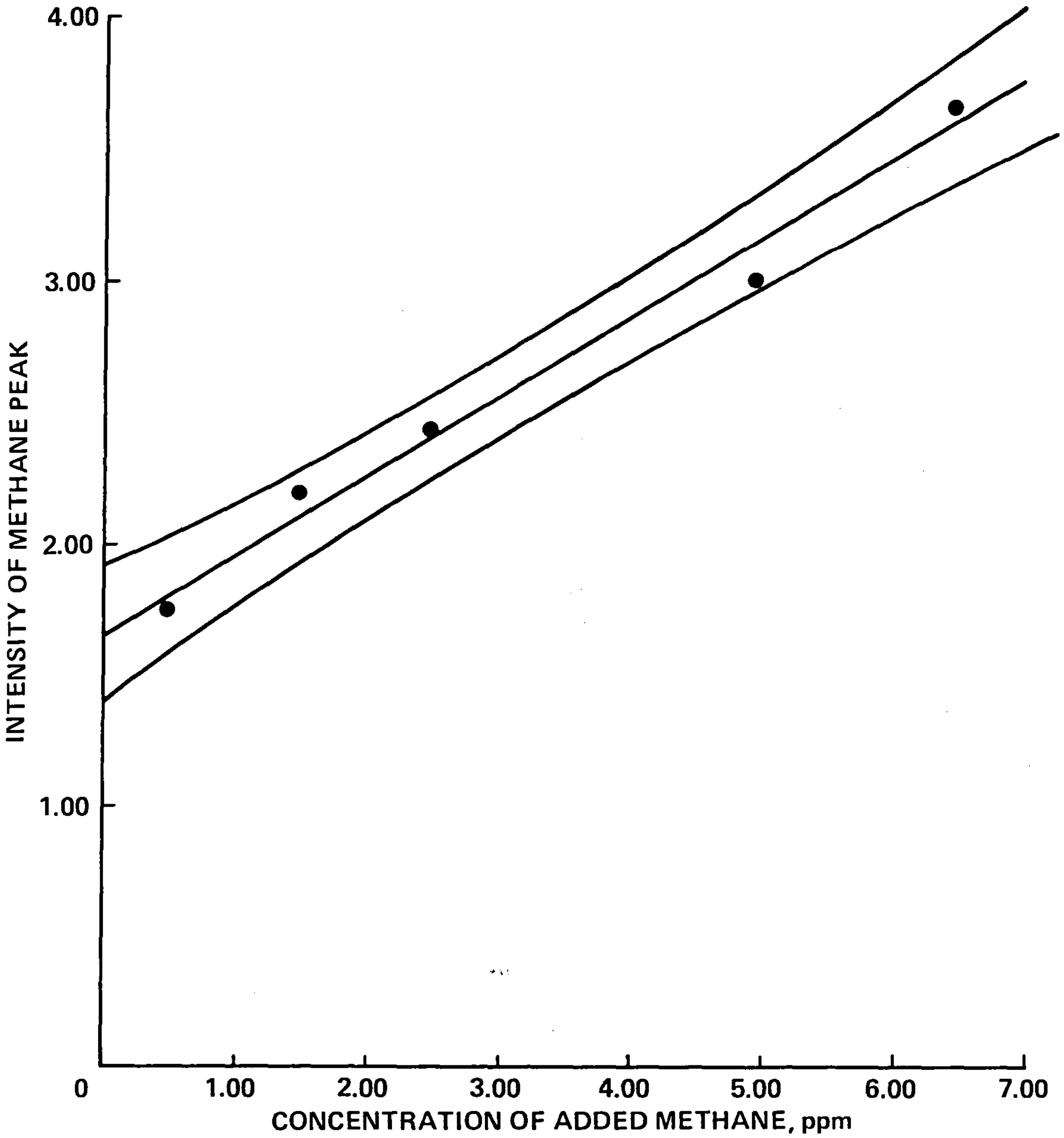

Figure 12

Calibration curve showing a linear increase in the intensity of the measured signal with increasing amounts (0.49 ppm to 6.42 ppm) of Methane added to ambient air. Each point represents 30.7 minutes of analysis and 105 modulation pulses. The coefficient of determination for this curve was found to be 0.99. The slope for the best straight line is 0.30 ± 0.02. The confidence bands are at a 3-sigma confidence level for the line as a whole (51).

TABLE I

Standard Additions Calibration Curve

1) Amplitude of the signal divided by the total number of data points (4608 points) obtained in each of the experiments for 30.7 minutes.
2) Concentration of added methane to ambient air.
3) Best value of the intensity in the best straight line obtained by the least square method.
4) Confidence levels at a 3-sigma confidence level for each of the points in the line (51).
5) Maximum and minimum values of intensity for each point at 3-sigma confidence level.

Y(Int/N)(1)	X(PPM)(2)	Yc(3)	Wl(4)	Yc+Wl(5)	Yc-Wl(5)
1.756	0.49	1.811	0.226	2.037	1.585
2.190	1.48	2.111	0.181	2.292	1.930
2.439	2.47	2.411	0.151	2.562	2.260
3.040	4.94	3.158	0.185	3.343	2.973
3.672	6.42	3.606	0.257	3.863	3.349

Consequently, calibration standards had to be run at a somewhat higher concentration than ambient methane concentrations. Therefore, we could only assume that the same calibration curve slope applies at ambient air methane concentrations and that the ambient air methane concentration did not change significantly during the short time period of the calibration. These assumptions seem reasonable based on the results obtained, however error could probably be reduced by introducing standards prior to the dryer.

Figure 13 is the lowest concentration chromatogram obtained during an eight day continuous determination of methane in ambient air. The measured concentration of methane in this sample period is 1.53 ± .60 ppm. Based on the signal-to-noise ratio of this chromatogram, the detection limit is about 1.0 ppm of methane. Since the noise is mostly due to remaining matrix effects, it is not random and could potentially be corrected to give a lower detection limit by subtracting a blank. This is not required because 1.0 ppm is already below the background concentration of methane in ambient air.

Figure 14 shows a profile of the average concentration of methane in ambient air in this laboratory for one hour increments during an eight day period. The data obtained for this profile is shown in Table II. Some data points are missing due to computer malfunctions. During this experiment, the concentration of methane varied from a low of 1.53 ± .60 ppm to a high of 4.63 ± .59 ppm. Methane concentration in the atmosphere is typically reported at 2 ppm (52,53). Measurements from aircraft have placed concentrations at 1.59 ppm over Saudi Arabia and 1.54 ppm over the Arabian Sea with some variation due to altitude (54,55). The lowest concentrations observed in this work are

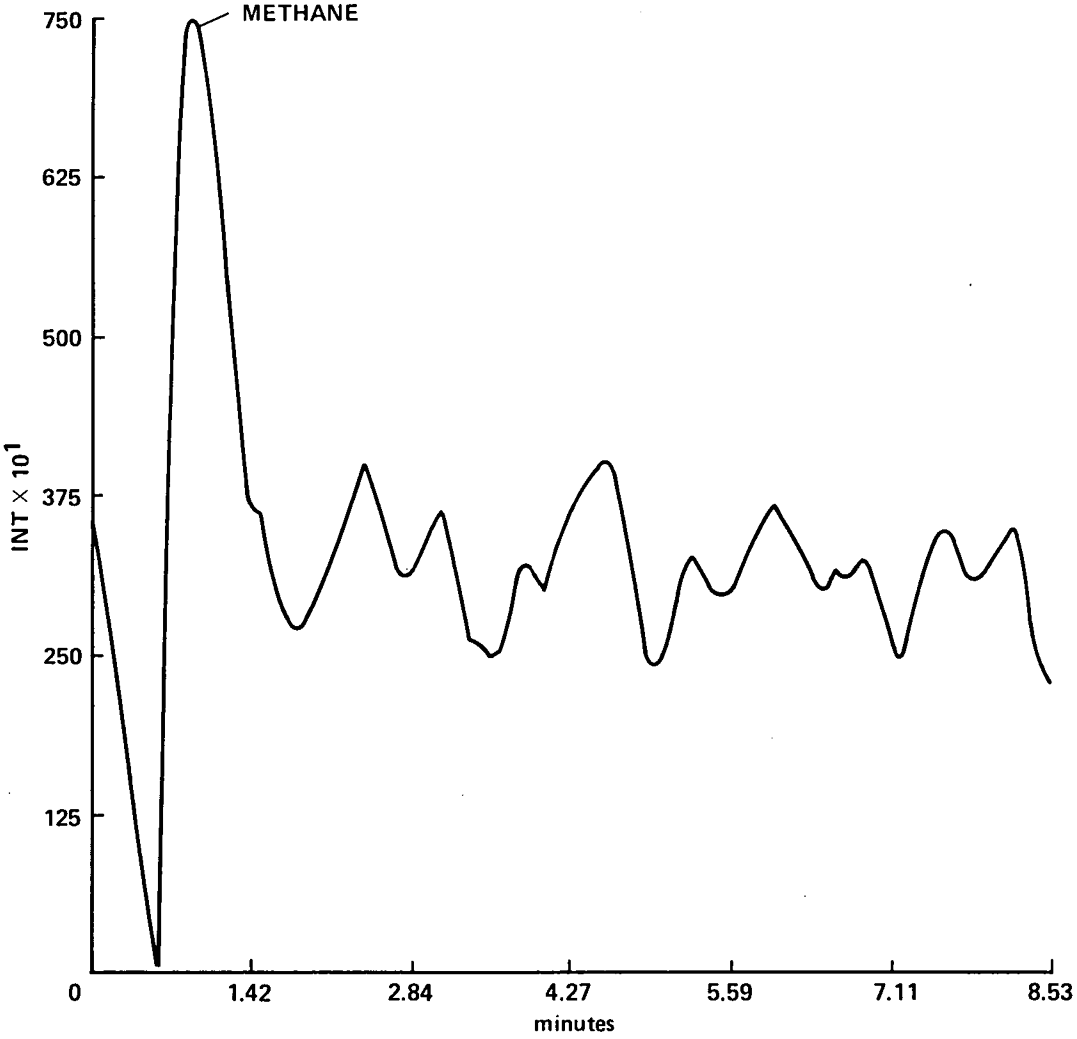

Figure 13

Chromatogram representing the lowest average concentration of Methane (1.53 ± .60 ppm) in ambient air for a one hour period obtained by cross-correlation of data taken during the 8-day experiment. Column temperature was 25 C and the flow rate was 14.0 sccm.

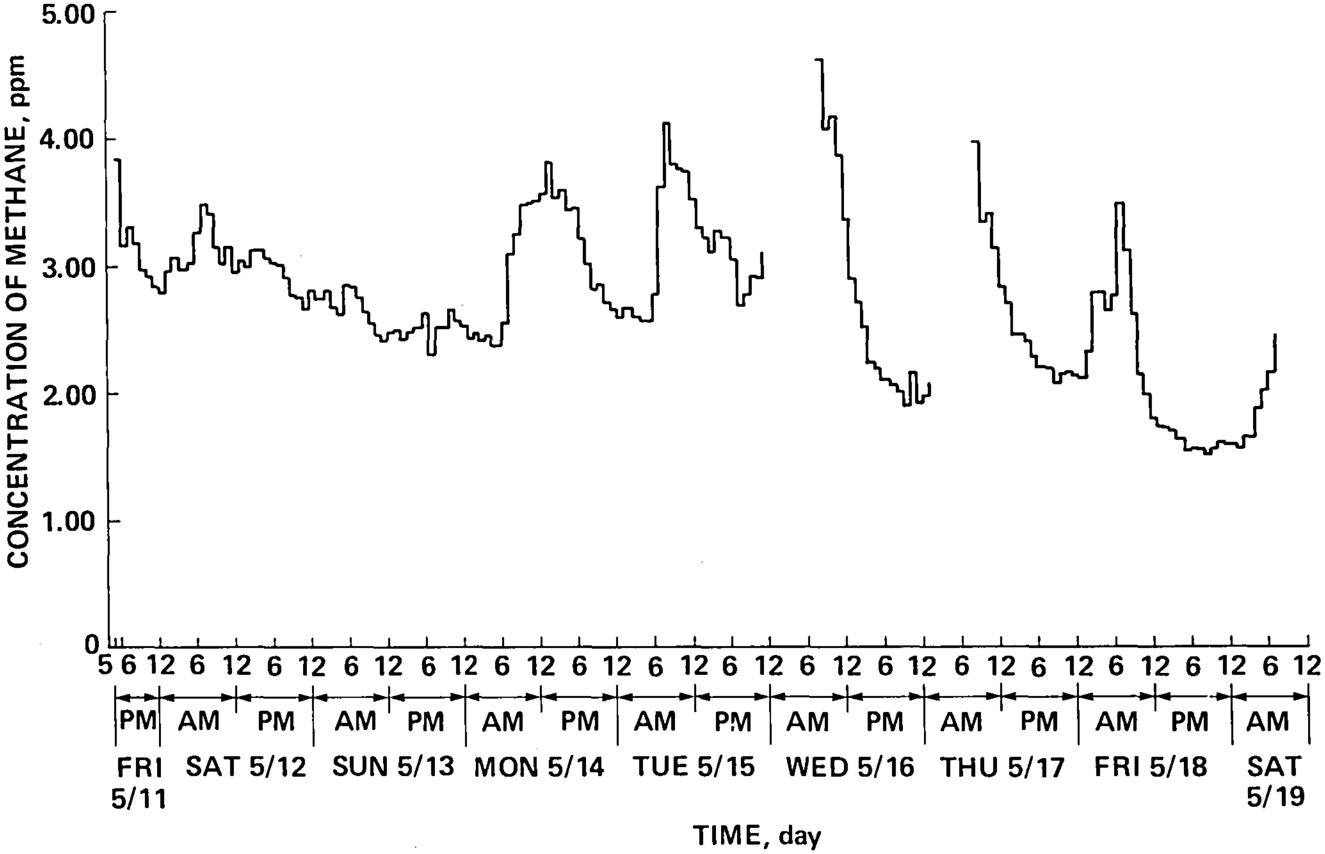

Figure 14

Profile of the concentration of Methane in ambient air showing one hour averages for an 8-day period. The experiment was started on Friday, May 11, 1984 at 5 p.m. and ended on Saturday, May 19, 1984 at 7 a.m. Some data points are missing due to computer malfunctions.

TABLE II

Experimental Data of the Profile of Methane in Ambient Air Obtained During Eight Days

Listing of the experimental data obtained for the monitoring of methane in ambient air during a period of 8 days. The data acquisition was started in Friday, May 11, 1984 at 5 PM and ended in Saturday, May 19, 1984 at 7 AM. This data is plotted in Figure 14. Each data pont represents an average of the data collected for about one hour. At first, it was intended to divide the data in sets of about 48 hours each because after each such period the A/D converter needs to be reset. During the third and fourth sets the 48 hours could not be completed because of computer malfunctions.

1) Date and day of the week.
2) Time when each determination was started.
3) The quotient of the intensity of the methane peak divided by the total number of data points (9216 points) collected for one hour.
4) Concentration of methane calculated from the calibration curve.
5) Confidence level at 3-sigma for the value of the methane concentration peak obtained from the calibration curve (51).

First Set

	DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	[]PPM(Y)(4)	W3(5)
1)	5/11/84,<u>FRI</u>	5:00.00,<u>PM</u>	1.164	3.84	0.58
2)		6:01.44	0.9580	3.16	0.57
3)		7:02.88	1.007	3.32	0.57
4)		8:04.32	0.9668	3.19	0.57

TABLE II (continued)

	DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	[]PPM(Y)(4)	W3(5)
5)		9:05.76	0.9023	2.98	0.57
6)		10:07.20	0.8843	2.92	0.57
7)		11:08.64	0.8641	2.85	0.57
8)	5/12/82,SAT	12:10.08,AM	0.8492	2.80	0.57
9)		1:11.52	0.8965	2.96	0.57
10)		2:12.96	0.9287	3.06	0.57
11)		3:14.40	0.9029	2.98	0.57
12)		4:15.84	0.9198	3.04	0.57
13)		5:17.28	0.9866	3.26	0.57
14)		6:18.72	1.055	3.48	0.57
15)		7:20.16	1.037	3.42	0.57
16)		8:21.60	0.9584	3.16	0.57
17)		9:23.04	0.9212	3.04	0.57
18)		10:24.48	0.9570	3.16	0.57
19)		11:25.92	0.8977	2.96	0.57
20)		12:27.36,PM	0.9233	3.05	0.57
21)		1:28.80	0.9093	3.00	0.57
22)		2:30.24	0.9491	3.13	0.57
23)		3:31.68	0.9486	3.13	0.57
24)		4:33.12	0.9311	3.07	0.57
25)		5:34.56	0.9223	3.04	0.57
26)		6:36.00	0.9120	3.01	0.57
27)		7:37.44	0.8854	2.92	0.57
28)		8:38.88	0.8460	2.79	0.57
29)		9:40.32	0.8353	2.76	0.58

TABLE II (continued)

	DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	[]PPM(Y)(4)	W3(5)
30)		10:41.76	0.8098	2.67	0.58
31)		11:43.20	0.8514	2.81	0.57
32)	5/13/84,<u>SUN</u>	12:44.64,<u>AM</u>	0.8347	2.75	0.58
33)		1:46.08	0.8531	2.82	0.57
34)		2:47.52	0.8116	2.68	0.58
35)		3:48.96	0.7983	2.63	0.58
36)		4:50.40	0.8666	2.86	0.57
37)		5:51.84	0.8635	2.85	0.57
38)		6:53.28	0.8378	2.76	0.58
39)		7:54.72	0.8035	2.65	0.58
40)		8:56.16	0.7755	2.56	0.58
41)		9:57.60	0.7480	2.47	0.58
42)		10:59.04	0.7375	2.43	0.58
43)		12:00.48,<u>PM</u>	0.7548	2.49	0.58
44)		1:01.92	0.7561	2.50	0.58
45)		2:03.36	0.7408	2.44	0.58
46)		3:04.80	0.7551	2.49	0.58
47)		4:06.24	0.7640	2.52	0.58

Second Set

	DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	[]PPM(Y)(4)	W3(5)
1)	5/13/84,<u>SUN</u>	5:30.00,<u>PM</u>	0.8004	2.64	0.58
2)		6:31.44	0.7004	2.31	0.58
3)		7:32.88	0.7644	2.52	0.58
4)		8:34.32	0.7676	2.53	0.58
5)		9:35.76	0.8097	2.67	0.58

TABLE II (continued)

DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	[]PPM(Y)(4)	W3(5)
6)	10:37.20	0.7827	2.58	0.58
7)	11:38.64	0.7732	2.55	0.58
8) 5/14/84,MON	12:40.08,AM	0.7429	2.45	0.58
9)	1:41.52	0.7514	2.48	0.58
10)	2:42.96	0.7324	2.42	0.58
11)	3:44.40	0.7464	2.46	0.58
12)	4:45.84	0.7256	2.39	0.58
13)	5:47.28	0.7768	2.56	0.58
14)	6:48.72	0.9378	3.10	0.57
15)	7:50.16	0.9864	3.26	0.57
16)	8:51.60	1.058	3.49	0.57
17)	9:53.04	1.060	3.50	0.57
18)	10:54.48	1.067	3.52	0.57
19)	11:55.92	1.081	3.57	0.57
20)	12:57.36,PM	1.157	3.82	0.58
21)	1:58.80	1.075	3.55	0.57
22)	3:00.24	1.094	3.61	0.58
23)	4:01.68	1.045	3.45	0.57
24)	5:03.12	1.051	3.47	0.57
25)	6:04.56	0.9787	3.23	0.57
26)	7:06.00	0.9215	3.04	0.57
27)	8:07.44	0.8601	2.84	0.57
28)	9:08.88	0.8669	2.86	0.57
29)	10:10.32	0.8296	2.74	0.58
30)	11:11.76	0.8086	2.67	0.58

TABLE II (continued)

	DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	PPM(Y)(4)	W3(5)
31)	5/15/84,TUE	12:13.20,AM	0.7902	2.61	0.58
32)		1:14.64	0.8106	2.68	0.58
33)		2:16.08	0.7922	2.61	0.58
34)		3:17.52	0.7840	2.59	0.58
35)		4:18.96	0.7847	2.59	0.58
36)		5:20.40	0.8465	2.79	0.57
37)		6:21.84	1.100	3.63	0.58
38)		7:23.28	1.254	4.14	0.58
39)		8:24.72	1.156	3.82	0.58
40)		9:26.16	1.144	3.78	0.58
41)		10:27.60	1.136	3.75	0.58
42)		11:29.04	1.074	3.54	0.57
43)		12:30.48,PM	1.005	3.32	0.57
44)		1:31.92	0.9812	3.24	0.57
45)		2:33.36	0.9441	3.12	0.57
46)		3:34.80	0.9956	3.28	0.57
47)		4:36.24	0.9796	3.23	0.57
		Third Set			
1)	5/15/84,TUE	6:00,PM	0.9284	3.06	0.57
2)		7:01.44	0.8182	2.70	0.58
3)		8:02.88	0.8453	2.79	0.58
4)		9:04.32	0.8881	2.93	0.57
5)		10:05.76	0.8813	2.91	0.57
6)		11:07.20	0.9415	3.11	0.57

TABLE II (continued)

DATE (1)	TIME (HR&MIN) (2)	INT/N (X) (3)	PPM (Y) (4)	W3 (5)
Fourth Set				
1) 5/16/84,WED	7:30.00,AM	1.403	4.63	0.59
2)	8:31.44	1.239	4.09	0.58
3)	9:32.88	1.270	4.19	0.58
4)	10:34.32	1.180	3.89	0.58
5)	11:35.76	1.024	3.38	0.57
6)	12:37.20,PM	0.8829	2.91	0.57
7)	1:38.64	0.8267	2.73	0.58
8)	2:40.08	0.7695	2.54	0.58
9)	3:41.52	0.6810	2.25	0.58
10)	4:42.96	0.6734	2.22	0.58
11)	5:44.40	0.6436	2.12	0.58
12)	6:45.84	0.6315	2.08	0.58
13)	7:47.28	0.6109	2.02	0.59
14)	8:48.72	0.5799	1.91	0.59
15)	9:50.16	0.6573	2.17	0.58
16)	10:51.60	0.5885	1.94	0.59
17)	11:53.04	0.6018	1.99	0.59
18) 5/17/84,THU	12:54.48,AM	0.6345	2.09	0.58
Fifth Set				
1) 5/17/84,THU	8:00.00,AM	1.209	3.99	0.58
2)	9:01.44	1.019	3.36	0.57
3)	10:02.88	1.035	3.42	0.57
4)	11:04.32	0.9551	3.15	0.57

TABLE II (continued)

DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	[]PPM(Y)(4)	W3(5)
5)	12:05.76,PM	0.8636	2.85	0.57
6)	1:07.20	0.8229	2.72	0.57
7)	2:08.64	0.7499	2.47	0.58
8)	3:10.08	0.7490	2.47	0.58
9)	4:11.52	0.7349	2.42	0.58
10)	5:12.96	0.6963	2.30	0.58
11)	6:14.40	0.6706	2.21	0.58
12)	7:15.84	0.6683	2.20	0.58
13)	8:17.28	0.6346	2.09	0.58
14)	9:18.72	0.6530	2.16	0.58
15)	10:20.16	0.6614	2.18	0.58
16)	11:21.16	0.6522	2.15	0.58
17) 5/18/84,FRI	12:23.04,AM	0.6446	2.13	0.58
18)	1:24.48	0.7105	2.34	0.58
19)	2:25.92	0.8482	2.80	0.57
20)	3:27.36	0.8474	2.80	0.57
21)	4:28.80	0.8065	2.66	0.58
22)	5:30.24	0.8422	2.78	0.58
23)	6:31.68	1.059	3.50	0.57
24)	7:33.12	0.9519	3.14	0.57
25)	8:34.56	0.7977	2.63	0.58
26)	9:36.00	0.6536	2.16	0.58
27)	10:37.44	0.6072	2.00	0.59
28)	11:38.88	0.5503	1.82	0.59
29)	12:40.32,PM	0.5312	1.75	0.59

TABLE II (continued)

	DATE(1)	TIME(HR&MIN)(2)	INT/N(X)(3)	[]PPM(Y)(4)	W3(5)
30)		1:41.76	0.5281	1.74	0.59
31)		2:43.20	0.5213	1.72	0.59
32)		3:44.64	0.5004	1.65	0.60
33)		4:46.08	0.4716	1.56	0.60
34)		5:47.52	0.4763	1.57	0.60
35)		6:48.96	0.4725	1.56	0.60
36)		7:50.40	0.4640	1.53	0.60
37)		8:51.84	0.4754	1.57	0.60
38)		9:53.28	0.4907	1.62	0.60
39)		10:54.72	0.4862	1.60	0.60
40)		11:56.16	0.4834	1.60	0.60
41)	5/19/84,SAT	12:57.60,AM	0.4794	1.58	0.60
42)		1:59.04	0.5020	1.66	0.60
43)		3:00.48	0.5039	1.66	0.59
44)		4:01.92	0.5739	1.89	0.59
45)		5:03.36	0.6194	2.04	0.59
46)		6:04.80	0.6598	2.18	0.58
47)		7:06.24	0.7511	2.48	0.58

comparable to the reported values indicating that the method gave reasonable results and the validity of the assumptions made during calibration is confirmed. The profile also shows many higher concentrations indicating the presence of some local source or sources of methane. An interesting temporal variability is apparent in this continuous measurement. Little variation is observed through the first few days, except for a general downward trend from a high of 3.84 ± .58 ppm to a low of 2.43 ± .58 ppm. There is a small peak of 3.48 ± .57 ppm on Saturday at 6:00 a.m., but it does not appear significant in the context of the adjoining days. At the onset of the work week, however, a series of rather large perturbations, up to as high as 4.63 ± .59 ppm, which center on mid to late morning, begin to appear and on Saturday the extent of this rise decreases to an amount comparable to the previous Saturday.

This data clearly shows evidence of some regular process, however, it has not been determined as yet whether the source of these perturbations are anthropogenic, natural or both as there are many potential methane sources in the immediate area. This laboratory resides beside two freeways in a highly urban area. It is situated near the San Francisco Bay and a large expanse of mud flats which are known to produce methane (56,57). Other workers from our laboratory have taken air samples 2 inches above the water in a hyper-saline pond in the adjoining bay marshes area and, using conventional gas chromatographic analysis of these samples, showed concentratios of 3.6 ± .2 ppm for methane (58). The laboratory shares the site with a Naval Air Station which has significant aircraft activity. There is a nearby facility where a local city manufactures methane in a sanitary landfill (59,60,61). Methane generation by methanogenic bacteria within sanitary landfills has been well documented and implicated in several fires and explosions (62). Of course, the local source could be within the laboratory itself. It is tempting to assign these daily variations in methane to activities associated with the work week since no appreciable variation in methane concentration is evident on Sunday, but many studies remain before a credible conclusion can be reached. For example, the mud flats could be solely responsible for these variations. They are susceptible to tidal cycles, water and air temperature, and influx of nutrients which vary daily, but are not related to anthropogenic activity. The data, thus far, does indicate that there is considerable temporal variation in methane concentration in the local ambient air and that continuous, long term monitoring can provide interesting insights into possible sources.

The system reported here has four sources of selectivity: 1) the dryer which removes all but the light gases from ambient air, 2) the modulator which catalyzes the oxidation of hydrocarbons, 3) the column which separates the gases according to their retention times, and 4) the detector which is sensitive only to oxidizable compounds. The only substance which is not restricted from being detected is methane. There is some redundancy in the selectivity and for this particular determination, the column could probably be eliminated. In future multiplex gas chromatography studies, it should be possible to take advantage of this selectivity by combining other specific modulators with specially chosen columns and other selective or non-selective detectors to determine many other specific substances.

This work has demonstrated the utility of a relatively simple multiplex gas chromatograph for the analysis of a real sample. The system reported here eliminates the need for any expendables other than power. Many more samples are analyzed, as compared to conventional gas chromatography. The operating mechanical components have very high reliability and no requirement for low dead volume is placed upon them. While a rather sophisticated laboratory computer was used to control the system and acquire data, any one of a number of inexpensive microprocessors could be substituted. By appropriate changes in columns, modulators, pretreatment devices and detectors this technique should be applicable to other components of ambient air, or possibly to process streams. In the long term, variations of this technique could be applied to the chemical analysis of the planetary atmospheres.

CHAPTER V

CONCLUSION

The basic technique of multiplex gas chromatography has been demonstrated using chemical modulators with only one gas stream consisting of the carrier in combination with the components being analyzed. This has resulted in a simplification of the instrument as well as in a reduction in the number of consumables required. It is possible to operate a gas chromatograph using no consumables beyond power. In addition to this, improvements in sensitivity and detection limits, up to 100-fold, have been achieved. The instruments designed made use of simple, rugged, and inexpensive components.

Concurrent with all these developments, the advantages of selectively modulating some of the components present in the sample, instead of all of them, have been demonstrated. Selective modulation should have applications analogous to selective detection. For some particular determinations, the column could even be eliminated.

While the long term goal of this study continues to be in the area of space exploration, interesting applications of this technique on Earth have also been found.

Suggestions for Future Research

Analytical challenges still exist in fugure NASA research projects. These missions include a comet rendezvous and atmospheric probes to Saturn, Titan, and Mars. In any space mission limitations in weight, available space, and costs, place strict requirements on the flight instruments. It has been demonstrated how multiplex gas chromatography can accommodate many of these restrictions. Further work must focus on developing more efficient and much faster modulators in order to obtain much more information in much shorter times. In the meantime, interesting applications on Earth can be found in the course of the research for the benefit of all of us.

CHAPTER VI

REFERENCES

1. Tswett, M. Ber. deut. botan. Ges. (1906), 24, 316, 384.
2. Laitinen, Herbert A.; Ewing, Galen W. "A History of Analytical Chemistry," The Division of Analytical Chemistry of the American Chemical Society: Washington, D.C., 1977: Chapter V.
3. Eucken, A.; Knick, H. Brennstoff-Chem. (1936), 17, 241-244.
4. Turner, N.C. Natl. Petroleum News (1943), 35 (18), R234-R237.
5. Claesson, S. Arkiv Kemi Mineral. Geol. (1946), 23A, 1-133.
6. Phillips, C.S.G. Disc. Faraday Soc. (1949), 7, 241-248.
7. Hesse, G.; Tschachotin, B. Naturwissenschaften (1942), 30, 387-392.
8. Cremer, E.; Muller, R. Mikrochim. Acta (1951), 36/37, 553-560.
9. Cremer, E.; Prior, F. Z. Elektrochem (1951), 55 (1), 66-70.
10. Janak, J. Chem. Listy. (1953), 47, 464-467.
11. Janak, J. Chem. Listy. (1955), 49, 1403-1405
12. Martin, A.J.P.; Singe, L. M. Biochem. J. (1941), 35, 1358-1368.
13. James, A. T.; Martin, A.J.P. Biochem. J. (proc.) (1951), 48, vii.
14. Grob, Robert L. "Modern Practice of Gas Chromatography," John Wiley & Sons: New York, 1977.
15. Oyama, Vance I.; Berdhal, Bonnie J. J. Geophys. Res. (1977), 82, 4669-4679.
16. Oyama, V. I.; Carle, G. C.; Woeller, F.; Rockling, S.; Vogrin, J.; Potter, W.; Rosiak, G.; Reichwein, C. IEEE Trans. Geosci. and Remote Sensing. (1980), GE-18, 85-93.

17. Tyson, Bennett J.; Carle, Glenn C. Anal. Chem. (1974), 46, 610-613

18. Pellizzary, E. D. "Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors," Research Triangle Institute, Research Triangle Park, NC, Environ. Prot. Agency (US), Rep. EPA-600/2-75-076 1975.

19. Phillips, J. B.; Burke, M.F. J. Chromatogr. Sci. (1976), 14, 495-497.

20. Annino, R.; Bullock, L. E. Anal. Chem. (1973), 45, 1221-1227

21. Villalanti, D. C.; Burke, M. F.; Phillips, J. B. Anal. Chem. (1979), 51, 2222-2225.

22. Annino, R.; Gonnard, M-F.; Guiochon. G. Anal. Chem. (1979). 51. 379-382.

23. Valentin, J. R.; Carle, G. C.; Phillips, J.B. J. High Resolut. Chromatogr. and Chromatogr. Comm. (1982), 5, 269-271.

24. Phillips, J. B. Anal. Chem. (1980), 52, 468A-478A.

25. Carney, D. P.; Phillips, J. B. J. High Resolut. Chromatogr. and Chromatogr. Comm. (1981), 4, 413-414.

26. Phillips, J. B.; Valentin, J. R.; Carle, G. C. "Toxic Materials in the Atmosphere," STP 786, American Society for Testing and Materials; Philadelphia, 1982, pp 135-141.

27. Wholler, F.; Kojiro, D.; Pollack, G. J. Chromatogr. Sci., (1982), 20, 176-181.

28. Valentin, J. R.; Carle, G. C.; Phillips, J. B. J. High Resolut. Chromatogr. and Chromatogr. Comm., (1983), 6, 621-622.

29. Lovelock, J. E. J. Chromatogr. (1975), 112, 29-36.

17. Tyson, Bennett J.; Carle, Glenn C. Anal. Chem. (1974), 46, 610-613

18. Pellizzary, E. D. "Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors," Research Triangle Institute, Research Triangle Park, NC, Environ. Prot. Agency (US), Rep. EPA-600/2-75-076 1975.

19. Phillips, J. B.; Burke, M.F. J. Chromatogr. Sci. (1976), 14, 495-497.

20. Annino, R.; Bullock, L. E. Anal. Chem. (1973), 45, 1221-1227

21. Villalanti, D. C.; Burke, M. F.; Phillips, J. B. Anal. Chem. (1979), 51, 2222-2225.

22. Annino, R.; Gonnard, M-F.; Guiochon. G. Anal. Chem. (1979). 51. 379-382.

23. Valentin, J. R.; Carle, G. C.; Phillips, J.B. J. High Resolut. Chromatogr. and Chromatogr. Comm. (1982), 5, 269-271.

24. Phillips, J. B. Anal. Chem. (1980), 52, 468A-478A.

25. Carney, D. P.; Phillips, J. B. J. High Resolut. Chromatogr. and Chromatogr. Comm. (1981), 4, 413-414.

26. Phillips, J. B.; Valentin, J. R.; Carle, G. C. "Toxic Materials in the Atmosphere," STP 786, American Society for Testing and Materials; Philadelphia, 1982, pp 135-141.

27. Wholler, F.; Kojiro, D.; Pollack, G. J. Chromatogr. Sci., (1982), 20, 176-181.

28. Valentin, J. R.; Carle, O. C.; Phillips, J. B. J. High Resolut. Chromatogr. and Chromatogr. Comm., (1983), 6, 621-622.

29. Lovelock, J. E. J. Chromatogr. (1975), 112, 29-36.

30. Ahurhovitskii, A. A.; Turkel'taub, N. M.; Gaier, M.; Lagashkina, M. N.; Malyasova, L. A.; Shlepuzhnikova, G. P. Zayodsk, Lab. (1963), 29 (1), 8-13.

31. Mellor, J. W. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, London, 1961, Vol. V, p. 817.

32. Valentin, J. R.; Carle, G. C.; Phillips, J. B. (Submitted to Analytical Chemistry).

33. Pollack, J. B. Icarus (1971), 14, 295.

34. Sagan, C.; Mullen, G. Science (1972), 177, 52-55.

35. Wang, W. C.; Yung, Y. L.; Lacis, A. A.; Mo, T.; Hansen, J. E. Science (1976), 194, 685-690.

36. Ehhalt, D. H.; Schmidt, U. Pure Applied Geophys. (1978), 116, 452-464.

37. Rasmussen, R. A.; Khalil, A. K. J. Geophys. Res. (1981), 86, 9826-9832.

38. Rasmussen, R. A.; Khalil, A. K. Atmos. Environ. (1981), 15, 883-886.

39. Rust, B. W.; Rothy, R. M.; Marland, G. J. Geophys. Res. (1979), 84, 3115-3121.

40. Smith, Mary Ann H., NASA Contract Rep CR 1982, NASA-TM-83289, NAS 1.15:83289, 71 pp. (Eng). Avail NTIS. From Sci. Tech. Aerosp. Rep. (1982), 20 (13), Abstr. No. N82-22822, Chem. Abstr. (1982), 97, 132567c.

41. Dianov-Klokov, V. I.; Lukshin, V. V.; Sklyarenko, I. Ya.; Shakula, Yu. P. Izv. Akad. Nauk SSSR, Fiz. Atmos. Okeana (1975), 11 (10), 993-998.

42. Moss, G. C.; Godfrey, K. R. Instrum. Technol. (1973), 20 (2), 33-36.

43. Evans, M. B.; Kawar, M. I.; Newton, R. Chromatographia (1981), 14 (7), 398-402.

44. Davey, Allan, Aust. J. Ecol. (1982), 7 (4), 395-401.

45. Robillard, M. V.; D'Alonzo, R. P.; Siggia, S.; Uden, P. C. J. Chromatogr. Sci. (1979), 17, 410-412.

46. Atroshehenko, V.I.; Gavrya, N. A.; Shchedrinskaya, Z. M. U.S.S.R. 132, 623, Oct. 20, 1960. Abstr. 55, 8823c.

47. Calvet, E.; Thibon, H. J. Chim. Phys. (1960), 57, 5-9.

48. Stevens, C. M.; Krout, L. Int. J. Mass Spectrom. Ion. Phys. (1972), 8, 265-275.

49. Swinnerton, J. W.; Linnebom, V. J.; Lamontague, R. A. Science (1970), 67, 984-986.

50. Bove, J. L.; Siebenberg, S. Science (1970), 67, 986-987.

51. Natrela, M. G., "Experimental Statistics, Nat. Bur. of Stand. Hand. 91", U.S. Dept. of Commerce, Washington, D.C., 1966, pp 5-11 - 5-19.

52. Weast, R. C., Ed., "Handbook of Chemistry and Physics," 64th ed., CRC Press, Inc., Boca Raton, FL, 1983-1984, p F-162.

53. Considine, D. M., Ed., "Van Nostrand's Scientific Encyclopedia," 5th ed., Van Nostrand Reinhold Company, New York, NY, 1976, p 55.

54. Newell, JR. E.; Condon, E. P.; Reichle, H. G., Jr. J. Geophys. Res. (1981), 86, 9833-9838.

55. Heidt, L. E.; Krasnec, J. P.; Lueb, R. A.; Pollock, W. H.; Henry B. E.; Crutzen, P. J. J. Geophys. Res. (1980), 85, 7329-7336.

56. Hutton, W. E.; ZoBell, C. E. J. Bacteriol. (1949), 58, 463-473.

57. Mancinelli, R. L.; Shulls W. A.; McKay, C. P. Appl. Environ. Microbiol. (1981), 42, 70-73.

58. McKay, Christopher, NASA-Ames Research Center, personal communication, Sept. 1984.

59. EMCON Associates, "State of the Art of Methane Gas Enhancement in Landfills," prepared for Argonne National Laboratory, Pacific Gas & Electric Company, and Southern California Gas Company, published by Argonne National Laboratory, Report ANL/CNSV-23, (June 1981), p 3-20.

60. EMCON Associates, "State of the Art of Landfill Gas Recovery" prepared for Argonne National Laboratory, Pacific Gas & Electric Company, and Southern California Gas Company, published by Argonne National Laboratory, Report ANL/CNSV-TM-85, (July 1981), p 101-107.

61. EMCON Associates, "The Controlled Landfill Project, First Annual Report: Construction and Operation" prepared for Argonne National Laboratory, Pacific Gas & Electric Company, and Southern California Gas Company, published by Argonne National Laboratory, (July 1982), Figure 1, p 72-92.

62. Martyny, J. W.; Kennerson, D.; Wilson, B.; Lott, C. E., Jr. J. Environ. Health (1979), 41, 194-197.

This Page Intentionally Left Blank

Appendix A

Computer Programs for Controlled Accessories

```
SCR # 90
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE ) OCTAL
162000 CONSTANT CIR  ( CONTROL & INTERRUPT REGISTER )
CIR 2+ CONSTANT SMR  ( STATE & MESSAGE REGISTER )
SMR 2+ CONSTANT IOR  ( INPUT/OUTPUT REGISTER )
IOR 2+ CONSTANT VSR  ( VECTOR SWITCH REGISTER )
2 CONSTANT CPU  ( BUS ADDRESS FOR CPU ON IEC11-A )
0 CONSTANT A/D  ( BUS ADDRESS FOR NAI MODEL 760 A/D CONVERTER )








-->

SCR # 91
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
: CIR@ CONSTANT ;CODE  ( TEST BIT IN CIR AND RETURN FLAG )
 S -) CLR, W () CIR BIT, NE IF, S () INC, ENDIF, NEXT, C;
: 0CIR CONSTANT ;CODE  ( CLEAR BIT IN CIR )
 W () CIR BIC, NEXT, C;
: 1CIR CONSTANT ;CODE  ( SET BIT IN CIR )
 W () CIR BIS, NEXT, C;
: SMR@ CONSTANT ;CODE  ( TEST BIT IN SMR AND RETURN FLAG )
 S -) CLR, W () SMR BIT, NE IF, S () INC, ENDIF, NEXT, C;
: 0SMR CONSTANT ;CODE  ( CLEAR BIT IN SMR )
 W () SMR BIC, NEXT, C;
: 1SMR CONSTANT ;CODE  ( SET BIT IN SMR )
 W () SMR BIS, NEXT, C;


-->
```

Appendix A (continued)

```
SCR # 92
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
1 1CIR 1SACS  ( SET SYSTEM CONTROL ACTIVE STATE )
1 0CIR 0SACS  ( CLEAR SYSTEM CONTROL ACTIVE STATE )
1 CIR@ SACS@  ( TEST SYSTEM CONTROL ACTIVE STATE )
2 CIR@ LON@  ( TEST LISTEN ONLY )
4 1CIR 1LASTB  ( SET LAST BYTE )
10 1CIR 1BDAC  ( SET BLOCK DAC )
10 0CIR 0BDAC  ( CLEAR BLOCK DAC )
10 CIR@ BDAC@  ( TEST BLOCK DAC )
20 1CIR 1RSV  ( SET REQUEST SERVICE )
40 1CIR 1MC  ( SET MASTER CLEAR )
100 1CIR 1INTE  ( SET INTERRUPT ENABLE )
100 0CIR 0INTE  ( CLEAR INTERRUPT ENABLE )
100 CIR@ INTE@  ( TEST INTERRUPT ENABLE )
200 CIR@ INT@  ( TEST INTERRUPT )
-->

SCR # 93
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
400 0CIR 0SCHGE  ( CLEAR STATE CHANGE )
400 CIR@ SCHGE@  ( TEST STATE CHANGE )
1000 CIR@ NRFD@  ( TEST NOT READY FOR DATA LINE )
2000 1CIR 1BSRQ  ( SET BLOCK SRQ )
2000 0CIR 0BSRQ  ( CLEAR BLOCK SRQ )
2000 CIR@ BSRQ@  ( TEST BLOCK SRQ )
4000 0CIR 0NOLAC  ( CLEAR NO LISTENER ACTIVE )
4000 CIR@ NOLAC@  ( TEST NO LISTENER ACTIVE )
10000 0CIR 0ILMSGE  ( CLEAR ILLEGAL MESSAGE )
10000 CIR@ ILMSGE@  ( TEST ILLEGAL MESSAGE )
20000 0CIR 0END  ( CLEAR END OF BLOCK )
20000 CIR@ END@  ( TEST END OF BLOCK )
40000 CIR@ SRQ@  ( TEST SERVICE REQUEST )
100000 0CIR 0DATAACC  ( CLEAR DATA ACCEPTED )
-->
```

Appendix A (continued)

```
SCR # 94
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
100000 CIR@ DATAACC@  ( TEST DATA ACCEPTED )
1 1SMR 1TCS  ( SET TAKE CONTROL ASYNCHRONOUSLY )
2 1SMR 1TCA  ( SET TAKE CONTROL SYNCHRONOUSLY )
4 1SMR 1GTS  ( SET GO TO STANDBY )
10 1SMR 1RPP  ( SET REQUEST PARALLEL POLL )
10 0SMR 0RPP  ( CLEAR REQUEST PARALLEL POLL )
10 SMR@ RPP@  ( TEST REQUEST PARALLEL POLL )
20 1SMR 1LTN  ( SET LISTEN )
40 1SMR 1LUN  ( SET LOCAL UNLISTEN )
100 1SMR 1SIC  ( SET SEND INTERFACE CLEAR )
200 1SMR 1SRE  ( SET SEND REMOTE ENABLE )
200 0SMR 0SRE  ( CLEAR SEND REMOTE ENABLE )
200 SMR@ SRE@  ( TEST SEND REMOTE ENABLE )
400 SMR@ CACS@  ( TEST CONTROLLER ACTIVE STATE )
-->

SCR # 95
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
1000 SMR@ CSBS@  ( TEST CONTROLLER STANDBY STATE )
2000 SMR@ CPPS@  ( TEST CONTROLLER PARALLEL POLL STATE )
4000 SMR@ TACS@  ( TEST TALKER ACTIVE STATE )
10000 SMR@ LACS@  ( TEST LISTENER ACTIVE STATE )
20000 SMR@ SIAS@  ( TEST INTERFACE CLEAR ACTIVE STATE )
40000 SMR@ SRAS@  ( TEST REMOTE ENABLE ACTIVE STATE )
100000 SMR@ SPAS@  ( TEST SERIAL POLL ACTIVE STATE )
: BUSSRESET 1MC 1SACS 1SIC 1SRE ;  ( INITIALIZE BUSS )

-->





```

Appendix A (continued)

```
SCR # 96
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
: TSTATE 4 - @ NFA COUNT 1- 7 AND TYPE ;
: S?TEST IF R TSTATE SPACE ENDIF ;
: STATES?  ( LIST ALL STATES CURRENTLY ACTIVE )
 CR ." CIR STATES = "
 SACS@ S?TEST LON@ S?TEST BDAC@ S?TEST INTE@ S?TEST
 INT@ S?TEST SCHGE@ S?TEST NRFD@ S?TEST BSRQ@ S?TEST
 NOLAC@ S?TEST ILMSGE@ S?TEST END@ S?TEST SRQ@ S?TEST
 DATAACC@ S?TEST
 CR ." SMR STATES = "
 RPP@ S?TEST SRE@ S?TEST CACS@ S?TEST
 CSBS@ S?TEST CPPS@ S?TEST TACS@ S?TEST LACS@ S?TEST
 SIAS@ S?TEST SRAS@ S?TEST SPAS@ S?TEST CR ;
: VSTATE  ( VERIFY THAT THE DESIRED STATE IS SET )
 0= IF ." ERROR, STATE NOT " R TSTATE CR QUIT ENDIF ;
-->

SCR # 97
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
: ICOM! ( BYTE ---   )  ( SEND COMMAND BYTE )
 CACS@ VSTATE ODATAACC IOR ! DATAACC@ VSTATE ;
: IDATA! ( BYTE ---   )  ( SEND DATA BYTE )
 TACS@ VSTATE ODATAACC IOR ! ;
: IDATA@ (   --- BYTE )  ( RECEIVE DATA BYTE )
 LACS@ VSTATE ODATAACC IOR @ 400 / 377 AND ;
: DAWAIT SACS@ VSTATE 0        ( WAIT FOR DATA ACCEPT FLAG )
 BEGIN 1- DUP 0= DATAACC@ OR UNTIL  ( LOOP UNTIL ACCEPTED )
 DROP DATAACC@ VSTATE ;       ( TIME OUT ERROR? )
: SRQWAIT SACS@ VSTATE 0  ( WAIT FOR SERVICE REQUEST )
 BEGIN 1- DUP 0= SRQ@ OR UNTIL  ( LOOP UNTIL REQUEST )
 DROP SRQ@ VSTATE ;        ( TIME OUT ERROR? )
: IDLE?                  ( CHECK IEC11-A INITIALIZATION )
 SACS@ VSTATE            ( MUST BE INITIALIZED )
 CACS@ VSTATE ;          ( MUST BE CONTROLLER ACTIVE ) -->
```

Appendix A (continued)

```
SCR # 98
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
: 1IDLE  ( RETURN IEC11-A TO IDLE STATE )
1TCA 77 ICOM!              ( SET NO LISTENERS )
137 ICOM! 1GTS 1TCA ;      ( SET NO TALKER )
: LISTEN ( DEVICE ---   ) ( SEND LISTENER BUSS ADDRESS )
37 AND 40 OR ICOM! ;
: TALK ( DEVICE ---  )     ( SEND TALKER BUSS ADDRESS )
37 AND 100 OR ICOM! ;
: SPOLL ( DEVICE ---  )    ( GET DEVICE SERIAL POLL STATUS )
030 ICOM!                  ( ENABLE SERIAL POLL )
TALK 1LTN 1GTS             ( SET UP FOR TRANSFER )
DAWAIT IDATA@              ( GET STATUS BYTE )
1TCS 031 ICOM! 1GTS ;      ( DISABLE SERIAL POLL )


-->

SCR # 99
( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
: SEND ( ADDRESS COUNT ---  )
0 DO DUP C@ IDATA! DAWAIT 1+ LOOP   ( SEND THE STRING )
DROP 15 IDATA! DAWAIT 12 IDATA! ;   ( SEND CR/LF )
: RECIEVE ( ADDRESS --- ADDRESS COUNT )
DUP BEGIN DAWAIT IDATA@ DUP 15 = 0= WHILE ( GET THE STRING )
OVER C! 1+ REPEAT          ( STORE STRING INTO BUFFER )
DROP DAWAIT IDATA@ DROP          ( IGNORE CR/LF )
OVER - ;





-->

```

Appendix A (continued)

```
SCR # 100
  0 ( IEEE 488 BUS CONTROL VIA IEC11-A INTERFACE - CONTINUED )
  1 : A/DSEND ( ADDRESS COUNT ---  )
  2  IDLE?                               ( CHECK STATES )
  3  A/D LISTEN CPU TALK           ( SET UP FOR TRANSFER )
  4  1GTS SEND 1IDLE ;                     ( SEND MESSAGE )
  5 : A/D"  ( SEND FOLLOWING STRING UP TO " TO A/D )
  6  42 STATE @ IF COMPILE (") WORD ( COMPILE RUN TIME CODE )
  7  HERE C@ 1+ ALLOT ?ALIGN COMPILE A/DSEND ( ADD OUTPUT CODE )
  8  ELSE WORD HERE COUNT A/DSEND ENDIF ;  ( DO IT DIRECTLY )
  9  IMMEDIATE
 10 : A/DREAD ( ADDRESS --- BYTE ADDRESS COUNT )
 11  IDLE? SRQWAIT        ( CHECK STATES & WAIT FOR REQUEST )
 12  A/D SPOLL SWAP         ( GET STATUS BYTE )
 13  RECIEVE 1IDLE ;       ( READ DATA STRING )
 14 0 VARIABLE A/DB 4 ALLOT 40 C, 40 C,
 15 : A/D. A/DB A/DREAD TYPE SPACE . CR ; DECIMAL
```

Appendix B

Computer Programs for Data Acquisition

```
SCR # 60
( RAND RAN NUM GEN ) OCTAL 0 VARIABLE TABL#
0 VARIABLE RANDT 176 ALLOT  ( NUMBER TABLE )
BLK @ DUP TABL# ! BLOCK 1600 + RANDT 200 CMOVE  ( INI TAB )
CODE RAND (  --- 8-BIT NUMBER )
 RANDT INCB, VS IF, 1 # RANDT MOVB, ENDIF, ( INCRMENT INDEX )
 RANDT RO MOVB,  ( GET CURRENT TABLE INDEX )
 RANDT RO I) R1 MOVB, R1 S -) MOV, ( MOVE BYTE TO STACK )
 36 # RO SUB,   ( INDEX FOR OTHER BYTE )
 LE IF, 177 # RO ADD, ENDIF, ( CHECK FOR TABLE WRAP AROUND )
 RANDT RO I) R1 MOVB,  ( GET SECOND TABLE BYTE )
 R1 S () XOR,  ( GENERATE NEW RANDOM NUMBER )
 S () RANDT RO I) MOVB,  ( PUT RESULT BACK INTO TABLE )
 177400 # S () BIC,  ( CLEAR UPPER BITS FROM RESULT )
NEXT, C; DECIMAL ;S
n.4YlrpJB4aoO(u8Yg$<C;p"dYG560:XgeW,To!);C4nk>kk
    <oLpR-Tn/7[oy!JAI6~5nd}_mss,<K%01KB/
                                        KM7y9\]?u.

SCR # 106
DECIMAL
16250 CONSTANT REF# 2 CONSTANT HEATOFF
REF# VARIABLE BIG#  1 CONSTANT HEATON
0 VARIABLE BKCNT REF# VARIABLE SML#
0 VARIABLE CROM 512 ALLOT 0 VARIABLE CNT
1326 VARIABLE SCRBLK 200 CONSTANT #TAUS
36 CONSTANT BLKS# : BLK# SCRBLK @ 2 * 1 - ;
 7 CONSTANT PROB! BLK# VARIABLE DBLK
0 VARIABLE AVE# 0 , 0 VARIABLE INJ#
0 VARIABLE ARRAY #TAUS 4 * ALLOT ARRAY #TAUS 4 * ERASE
: A/D# A/DB 8 BLANKS A/DB A/DREAD ROT DROP DROP NUMBER ;
: SMALL! DUP SML# @ < IF DUP SML# ! ENDIF ;
: BIG! DUP BIG# @ > IF DUP BIG# ! ENDIF ;
: STOP@ DUP 1 < IF . CR ." BLK# " BKCNT ? A/D" A 0"
A/D" E" QUIT ENDIF DUP 32500 > IF . CR ." BLK# "
BKCNT ? A/D" A 0" A/D" E" QUIT ENDIF ; -->
```

Appendix B (continued)

```
SCR # 107
0 VARIABLE DPTR 0 VARIABLE DISKF
: DISK! DISKF @ IF ( STOP@ ) SMALL! BIG! OR CNT @
CROM + ! 2 CNT +! CNT @ 512 = IF BKCNT ? CROM ?
CROM DBLK @ DUP 1+ DBLK ! DUP . 0 I/O
0 CNT ! 1 BKCNT +! CR ENDIF ELSE DROP DROP ENDIF ;
HEX : DRIFT
2DUP AVE# 2@ D+ DPTR @
ARRAY + 2@ DABS DMINUS D+ AVE# 2! ROT
IF DMINUS ENDIF DPTR @ ARRAY + 2!
DPTR @ #TAUS 2* + #TAUS 4 * MOD ARRAY + 2@ DUP
0< IF DMINUS 8000
ELSE 0 ENDIF ROT ROT DPTR @ 4 +
DUP #TAUS 4 * = IF DROP 0 1 DISKF ! ENDIF DPTR ! ;


-->

SCR # 108
HEX : COLL A/D# DRIFT AVE# 2@ #TAUS M/MOD ROT
DROP DMINUS D+ DROP REF# + DISK! ;


: COOL-MOD A/D" A 010000" HEATOFF 0 DO 0
COLL LOOP A/D" A 010000" ;
: MOD-ON A/D" A 100000" HEATON
0 DO 8000 COLL
( I 9 = IF 8000 COLL ELSE 0 COLL ENDIF )
LOOP COOL-MOD ;





-->
```

Appendix B (continued)

```
SCR # 109
: CROMDAT! A/D" B" A/D# A/D" A 010000"


 BEGIN RAND PROB! < IF ( A/D" A 0" 0 COLL )
1 INJ# +! INJ# ? MOD-ON ENDIF
0 COLL  BKCNT @  BLKS# < 0= UNTIL A/D" E" A/D" A 010000"
CR ." SMALL#= " SML# ? CR ." BIG#= " BIG# ?
CR  ." POINTS " CR INJ# ? ." INJECTIONS " CR
BLKS# . ." BLOCKS " CR ." SCR# " SCRBLK @ DUP . CR
2* 1 - ." REC# " . CR ." 5 PPM SAMPLE " CR ; DECIMAL
: DEL&ST A/D" S 50" A/D" B" 0 DO A/D# D. CR LOOP ;
( A/D" S 04" 100 0 DO A/D# D. CR LOOP ; )
```

Appendix C

Computer Program for Cross-Correlation Computation

```
SCR # 110
DECIMAL ( CORR CALCS.,ARRAYS,VARIABLES&CONSTANTS )
1280 CONSTANT #TAUS #TAUS 4 * CONSTANT BTS
0 VARIABLE CCINPUT #TAUS ALLOT CCINPUT #TAUS ERASE
0 VARIABLE RTAU BTS ALLOT RTAU BTS ERASE
0 VARIABLE CROM 512 ALLOT
256 VARIABLE CNT 0 VARIABLE INJV
0 VARIABLE DBLK #TAUS CONSTANT TAUS
CCINPUT TAUS + 1- CONSTANT CCIEND 0 VARIABLE INJ#
( 0 VARIABLE CORREF 0 , ) 750 CONSTANT DATSCR
36 CONSTANT BLKS# 0 VARIABLE BKCNT
0 VARIABLE REFADJ -1 VARIABLE REFCNT -1 VARIABLE REFCNT#
16250 VARIABLE REF# 0 VARIABLE CALC#
: DRIFT 1 REFCNT +! REFCNT @ 0= IF
REFCNT# @ REFCNT ! REFADJ @ REF# +!
ENDIF ; 120 2* 2381 + 1- VARIABLE REC#
-->

SCR # 111
HEX : SEPDAT DUP 0< DUP IF 1 INJ# +! DROP
INJV @ DUP 1 < IF -1 INJ# +! DROP
0 ENDIF 0 INJV ! 1 MIN DUP . ENDIF CCINPUT 1+ CCINPUT
TAUS CMOVE CCIEND C! 7FFF AND REF# @ ( 10 / ) - 1 INJV +! ;
: DISK@ CNT @ 100 = IF CR BKCNT ? CROM
DBLK @ DUP DUP . 1+ DBLK ! 1 I/O 0 CNT ! 1 BKCNT +!
CROM ? RTAU 2@ D. 0 0 100 0 DO CROM I 2* + @ 7FFF AND REF#
@ - S->D D+ LOOP 2DUP D.
100 M/ SWAP DROP DUP DUP . 0< IF -1 ELSE 1 ENDIF REFADJ !
ABS 1 MAX 200 SWAP / MINUS -1 MIN REF# ? REFCNT# ! ENDIF
CROM CNT @ 2* + @ 1 CNT +! ; DECIMAL
: BLK# DATSCR 2* 1- DBLK ! ;
: NEWLN 10 MOD 0= IF CR ENDIF ;
CODE M+! S () W MOV, 2 S I) W )+ ADD,
W () ADC, 2 S I) ASL, W () SBC,
4 # S ADD, NEXT, C; -->
```

Appendix C (continued)

```
SCR # 112
( 0 VARIABLE AUTOCOR 2560 ALLOT 2560 ERASE ) DECIMAL
( : IN*IN! CCIEND 1+ CCINPUT DO I ( CALC AUTOCORR )
( C@ IF CCIEND I - 2* AUTOCOR + 1 +! ENDIF LOOP ; )
: IN*OUT! ( CCIEND C@ IF IN*IN! ENDIF ( CALC CROSSCORR )
CCIEND 1+ CCINPUT DO I C@ IF DUP I C@ 4 */ CCIEND
I - 4 * RTAU + M+! ENDIF LOOP DROP ;
: COMPUTE ( FETCH DAT & CALC AUT&CROS-COR )
BLK# -1 DISK@ DUP SEPDAT REF# +! BEGIN
OVER CCINPUT C@ AND IF SWAP 1+ SWAP ( RTAU BTS ERASE ) ENDIF
SEPDAT DRIFT IN*OUT! DISK@ BKCNT @ BLKS# > UNTIL 0 CNT ! ;
: DISK! ( WRITE BKS OF DAT TO DK ) CNT @ 512 =
IF REC# ? CROM REC# @ DUP 1 + REC# !
0 I/O 0 CNT ! ENDIF ;


-->

SCR # 113
DATSCR 2* 36 + 1- CONSTANT CALCREC
: CORCALC! ( COP DAT TO BKS )
( RTAU 2@ CORREF 2! ) TAUS 0 DO RTAU I 4 *
+ 2@  ( CORREF 2@ DMINUS D+ ) CNT @ CROM + 2!
4 CNT +! DISK! LOOP ;
( 90 LOAD )
: CALCULATE COMPUTE CORCALC! CR INJ# ? ." INJECTS " CR
." FIRST REC# " CALCREC . CR
." DATSCR# " DATSCR . CR ( A/D" A 1100" ) ;




: LISTCC 256 0 DO I 2 * CROM + @ . I NEWLN LOOP ;

```

Appendix D

Computer Program for Plotting Chromatogram

```
C COMMON BLOCK FOR MULTIPLEX GC PROGRAMS
C
        DIMENSION ICB(256,20)
C
        INTEGER FILSPC(39),DEFTYP(4),XD,XI
        DATA DEFTYP/3RCOR,3RPLT,3RPLT,3RPLT/
        REAL RCB,RXD,RXI,RXO,MRN
C
C CONVERSE WITH USER
C
10      TYPE 20
20      FORMAT(' ENTER DEVICE/FILE NAMES,OUTFILE=INFILE '/ )
        IF(ICSI(FILSPC,DEFTYP,,,0).NE.0) GOTO 10
        IF(IASIGN(8,FILSPC(16),FILSPC(17),0,4).NE.0) STOP 'INPUT FILE'
        IF(IASIGN(9,FILSPC(1),FILSPC(2),-1).NE.0) STOP 'OUTPUT FILE'
        TYPE 22
22      FORMAT(' RECORD NUMBER?, INT '/)
        ACCEPT *,IREC
        TYPE 24
24      FORMAT(' HOW MANY BLOCKS?, INT '/)
        ACCEPT *,IBLK
        NEXT=IREC
        DEFINE FILE 8 (0,256,U,NEXT)
        DO 25 I=1,IBLK
        READ(8'NEXT)(ICB(J,I),J=1,256)
25      CONTINUE
C CHOOSE THE BIGGEST AND SMALLEST NUMBER
        PX=-2147483648.
        PN=2147483647.
        DO 38 I=1,IBLK
C       TYPE 31,I
C 31    FORMAT(' '/' I= ',I6/)
        DO 37 J=1,255,2
        XD=ICB(J,I)
        XI=ICB(J+1,I)
        RXD=1.0*XD
        IF(XD.LT.0) RXD=32768.0+1.0*(1+XD+32767)
        RXI=1.0*XI
        RCB=(RXD+((RXI)*(16.0**4)))
```

Appendix D (continued

```
        IF(RCB.GT.PX) PX=RCB
        IF(RCB.LT.PN) PN=RCB
37      CONTINUE
38      CONTINUE
        TYPE 39,PN,PX
39      FORMAT(' SMALLEST#= ',F15.4,3X,/,' BIGGEST#= ',F15.4/)
40      TYPE 50
50      FORMAT(' PLOT RANGE? '/)
        ACCEPT *,ITN,ITX
60      TYPE 70
70      FORMAT(' PLOT SCALE? '/)
        ACCEPT *,PN,PX
C
C
C INITIALIZE PLOTTER
C
        CALL PLOTF(30,9)
        CALL SLINE
        CALL PLOT(.5,.5,-3)
        TYPE 72
72      FORMAT(' LENGTH & WIDTH OF PAPER? ONE IS
     18.5" X 11.", REAL '/)
        ACCEPT *,XL,YW
        X=XL/(ITX-ITN)
        Y=YW/(PX-PN)
        N=3
C
C PLOT DATA
C
        TYPE 160
160     FORMAT(' DATA TYPED?, 1=YES, 0=NO '$)
        ACCEPT *,KYES
        KTX=1
        DO 210 I=1,IBLK
        TYPE 171,I
171     FORMAT(' '/' I= ',I6/)
        DO 200 J=1,255,2
        XD=ICB(J,I)
        XI=ICB(J+1,I)
```

```
          RXD=1.0*XD
          IF(XD.LT.0) RXD=32768.0+1.0*(1+XD+32767)
          RXI=1.0*XI
          RCB=(RXD+((RXI)*(16.0**4)))
          IF(KYES.EQ.0) GO TO 175
          TYPE 173,RCB
 173      FORMAT('+RCB= ',F15.4,3X,$)
          JK=J-1
          IF(MOD(JK,10).EQ.0) TYPE 174
 174      FORMAT(' '/)
 175      IF(RCB.GT.PX) RCB=PX
          IF(RCB.LT.PN) RCB=PN
          CALL PLOT(KTX*X,(RCB-PN)*Y,N)
          KTX=KTX+1
            N=2
 200      CONTINUE
 210      CONTINUE
          TYPE 214
 214      FORMAT(' '/)
          TYPE 215
 215      FORMAT(' DATA PRINTED?, 1=YES,0=NO '$)
          ACCEPT *,IYES
          IF( IYES. EQ. 0) GO TO 300
 250      DO 260 I=1,IBLK
          PRINT 252,I
 252      FORMAT(' I= ',I6/)
          DO 258 J=1,255,2
          XD=ICB(J,I)
          XI=ICB(J+1,I)
          RXD=1.0*XD
          IF(XD.LT.0) RXD=32768.0+1.0*(1+XD+32767)
          RXI=1.0*XI
          RCB=(RXD+((RXI)*(16.0**4)))
          PRINT 254,RCB
 254      FORMAT('+RCB= ',F15.4,3X,$)
          JK=J-1
          IF(MOD(JK,8).EQ.0) PRINT 255
 255      FORMAT(' '/)
 258      CONTINUE
```

Appendix D (continued)

```
260     CONTINUE
C TERMINATE
C
C DRAW X & Y AXIS
300     TYPE 310
310     FORMAT(' HOW MANY SEC./PT. IN EXP.?, REAL '/)
        ACCEPT *,XSEC
        TYPE 312
312     FORMAT(' UNITS OF TIME IN MINUTES OR SECONDS?,
     11=MINUTES, 0=SECONDS, INT. '/)
        ACCEPT *,YMIN
        TYPE 314
314     FORMAT(' HOW MANY SKIPPED POINTS?,IF NONE TYPE 1,INT '/)
        ACCEPT *,ISKP
        XTX=ISKP*XSEC*ITX/XL
        IF(YMIN.EQ.1) XTX=XTX/60.0
        XTN=1.0*ITN
        YPN=0.0*PN
        YPX=(PX-PN)/YW
        CALL AXIS(XTN,YPN,' INT. ',4,YW,90.,YPN,YPX)
        IF(YMIN.EQ.1) GO TO 350
        GO TO 390
350     CALL AXIS(XTN,YPN,' MIN. ',-7,XL,0.,XTN,XTX)
        GO TO 400
390     CALL AXIS(XTN,YPN,' SEC. ',-7,XL,0.,XTN,XTX)
400     CALL PLOT(XL,-10.,-3)
        CALL POFF
        TYPE 410
410     FORMAT(' PLOT COMPLETE. '$)
        CALL EXIT
        STOP
        END
```

1. Report No. NASA TM-86668	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle MULTIPLEX GAS CHROMATOGRAPHY FOR USE IN SPACE CRAFT		5. Report Date January 1985
		6. Performing Organization Code
7. Author(s) Jose R. Valentin		8. Performing Organization Report No. 85065
9. Performing Organization Name and Address Ames Research Center Moffett Field, CA 94035		10. Work Unit No.
		11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Memorandum
		14. Sponsoring Agency Code 199-50-42

15. Supplementary Notes

Point of Contact: Jose R. Valentin, Ames Research Center, MS 239-12,
Moffett Field, CA 94035 (415) 694-5766 or FTS 464-5766

16. Abstract

Gas chromatography is a powerful technique for the analysis of gaseous mixtures. Some limitations in this technique still exist which can be alleviated with multiplex gas chromatography (MGC). In MGC, rapid multiple sample injections are made into the column without having to wait for one determination to be finished before taking a new sample. The resulting data must then be reduced using computational methods such as cross-correlation.

In order to efficiently perform multiplex gas chromatography, experiments in the laboratory and on board future space craft, skills, equipment, and computer software were developed. Three new techniques for modulating, i.e., changing, sample concentrations were demonstrated by using desorption, decomposition, and catalytic modulators. In all of them, the need for a separate gas stream as the carrier was avoided by placing the modulator at the head of the column to directly modulate a sample stream. In these modulators, an improvement in sensitivity of up to 100-fold was demonstrated. Also, the advantage of selective modulation was demonstrated. Selective modulation is potentially as valuable as selective detection. Finally, the analysis of an environmental sample by multiplex chromatography was accomplished by employing silver oxide to catalytically modulate methane in ambient air.

17. Key Words (Suggested by Author(s)) Tin oxide detector, Decomposition modulator, Desorption modulator, Catalytic modulator, Silver oxide, Ambient air carrier gas, Methane in ambient air, Cross-correlation	18. Distribution Statement Unlimited Subject Category - 25		
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 92	22. Price* A05

*For sale by the National Technical Information Service, Springfield, Virginia 22161

End of Document